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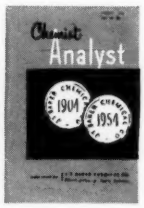

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VOLUME 32

February, 1955

NUMBER 2

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Subscription Price: Domestic $3.50 per year; Countries in Pan-American Union $3.50 per year; Canada $4.00; other countries $4.50. Issued monthly. Single copies of issues in current year, 50¢ each; all other single copies, one dollar. Foreign remittances must be accompanied by International Money Order.

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The JOURNAL OF CHEMICAL EDUCATION is the official organ of the Divisions of Chemical Education and History of Chemistry and incorporates the Report of the New England Association of Chemistry Teachers, and the Proceedings of the Pacific Southwest Association of Chemistry Teachers. It is indexed in the Education Index, Industrial Arts Index, and, in part, in the Quarterly Cumulative Index Medicus.

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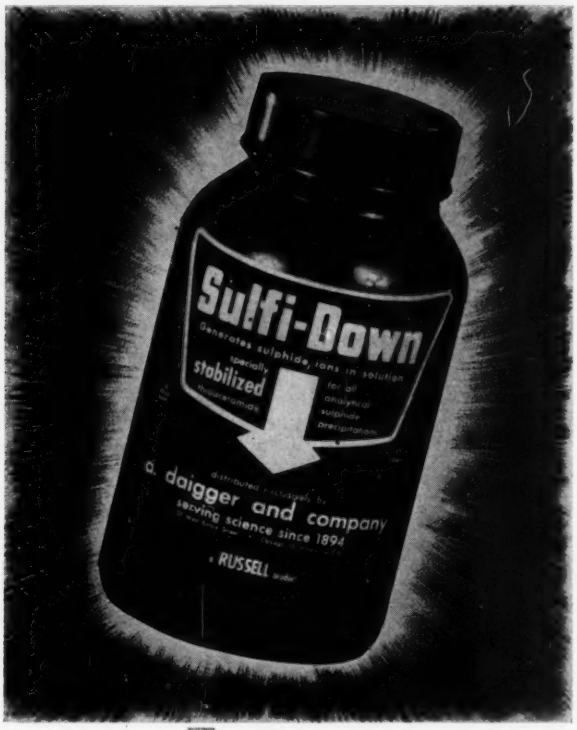

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DETACH SHEET BY CUTTING ALONG THIS LINE—PUNCH HOLES AND REINFORCE WITH GUMMED LINEN REINFORCEMENTS

2. OXYGEN*

A. OCCURRENCE

2-1 **Exhibit:** oxides, carbonates, sulfates, silicates.

*2-2 **Demonstrate:** air boxes.

2-3 Mg ribbon, tongs, burner. **Burn Mg. Forms MgO and a little Mg_3N_2. Shows oxygen is in air.**

B. PREPARATION OF OXYGEN

2-4. HgO, test tube, burner, splint. See 1-11. **Recall Priestley's and Lavoisier's classical experiments.**

*2-5 See figure. $KClO_3$. Two-hole stopper, from one hole a delivery tube leading into a 1-liter cylinder of water, from other an L-shaped tube 10 cms. long containing MnO_2. **Show bubbling O_2 from molten $KClO_3$. Remove burner. As soon as O_2 stops coming off, turn tube so as to dump MnO_2 into $KClO_3$, and O_2 again bubbles off, showing catalytic effect of MnO_2.**

2-6. Test tube, dropper-bottle of water, Na_2O_2, splint. **Test O_2 off. Note yellow flame due to Na.**

2-7. Test tube, MnO_2, H_2O_2, splint. **Show O_2 off, catalysis.**

2-8. Electrolysis of water apparatus. **See 1-4.**

2-9. Liquid air, 1-liter cylinder of water, splint. **Pour on water. When N_2 (sp. gr. 0.8, B.P. −195.8°C.) boils away, the remaining oxygen (sp. gr. 1.14, B.P. −183.0°C.) sinks into the water as drops of liquid, and O_2 gas makes glowing splint burst into flame.**

C. REACTIONS OF OXYGEN GAS

2-10. Sulfur, 1-liter cylinder of O_2, deflagrating spoon, burner, litmus paper. **Burn S, test with moist litmus paper.**

2-11. Red phosphorus, 1-liter cylinder of O_2, deflagrating spoon, burner, litmus paper. **Burn P, test with moist litmus paper.**

*2-12 Carbon, forceps, cylinder of O_2, burner. **Burn C.**

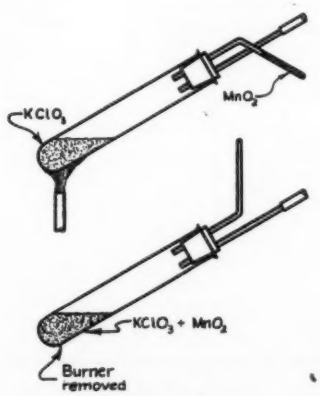


Figure 2-5

D. SOME OXIDATIONS

2-13 Steel wool loosely packed in upper quarter of a Dumas Tube (tube 6 × 50 cms.) of air inverted over water. **During the week steel rusts, water rises 1/5th up.**

*2-14 Candle on cork, 20 cm. crystallizing dish quarter-full of limewater, 800 ml. beaker. **Float lighted candle. Cover with beaker. The limewater becomes milky and the level of liquid inside the beaker rises as the CO_2 is absorbed.**

Turn the page for additional demonstrations

* Footnotes

2-2 Make a nest of wooden boxes of the following outside dimensions, and label them, illustrating composition of air by volume inhaled in 10 seconds. AIR-100%, a box 16 × 16 × 16 cms. N_2-78%, a box 14 × 10.5 × 14 cms. O_2-21%, a box 14 × 14 × 2.6 cms. A piece of 3/8" plywood 11 × 8 cms. to which round corks are glued to represent the following components: Argon-0.95%, 3 cms. diameter; CO_2-0.03%, 1.6 cms.; Ne-0.0018%, 0.5 cms.; He-0.0005%, 0.2 cms.; and spots for Kr-0.0001% and Xe-0.000009%.

2-12 If liquid air is available, burn a heated lump of charcoal the size of a pea in liquid air from which the N_2 has evaporated.

2-14 Repeat this experiment using water instead of limewater. Observe carefully why the water still rises up, remembering that (a) the candle does not combine with all of the O_2 present, (b) the formation of CO_2 from O_2 does not give a volume change since little CO_2 is absorbed, and (c) the water rises up but not exactly one-fifth.

2-15. CARE. Prepare the P in CS_2 the day of the lecture. Place in a safe location. Burns by it are severe; in case of accident keep the burned member soaked with 3% $CuSO_4$-aq. until treated by a physician.

2-17 See figure. Fit lid tightly for maximum effect. Dry flour can be substituted for, but is not so effective as lycopodium.

2-18 To prepare pyrophoric lead, gently heat about 10 grams lead tartrate in an 18 × 150 mm. test tube to complete charring. Immediately stopper. This keeps indefinitely, but ignites spontaneously when shaken into the air. The lead tartrate can be prepared by mixing a hot solution containing 70 g. Rochelle salt in 100 ml. water with one containing 60 g. $Pb(NO_3)_2$ in 100 ml. water. Cool, filter, press between filter papers. A shower of sparks can be obtained by (a) unstoppering tube and pouring out contents, (b) pouring contents on a sheet of paper, stirring with a spatula, and then allowing it to slide off the paper, or (c) (CARE) putting on the palm of hand and allowing material to slide off.

Labels for Topic 2. (For code, see instructions for assembling kits.) 2-3-*w*-Mg ribbon, 2-4-*w*-HgO, 2-5-*w*-$KClO_3$, 2-5-*w*-MnO_2, 2-6-*N*-Na_2O_2, 2-6-*d*-water, 2-7-*w*-MnO_2, 2-7-*n*-3% H_2O_2, 2-10-*w*-sulfur, 2-11-*w*-red P, 2-12-*w*-lumps of carbon, 2-13-*J*-steel wool, 2-14-*J*-candles, 2-14-*N*-limewater, 2-15-*N*-CS_2, 2-15-*N*-3% by wt. $CuSO_4$ aq. for phosphorus burns, 2-16-*w* with shaker top-iron filings, 2-17-*w*-lycopodium, 2-18-*w*-lead tartrate, 2-18-*J*-four tubes of pyrophoric lead. Also *J*: splints for 2-4, 2-5, 2-6-, 2-7, and 2-9.

* By Hubert N. Alyea, Frick Chemical Laboratory, Princeton, New Jersey. February, 1955

DETACH SHEET BY CUTTING ALONG THIS LINE—PUNCH HOLES AND REINFORCE WITH GUMMED LINEN REINFORCEMENTS

*2-15 *Some Kindling Temperatures: P=27, CS_2 =240, H_2=550°C.*

A piece of white phosphorus the size of a pea (CARE in handling) dissolved in 5 ml. CS_2; sheet of paper; an $H_2 + O_2$ bottle (see 1-7), burner, 6″ square of asbestos, 10 cm. evaporating dish, 0–250° thermometer, CS_2. **Show different kindling temperatures by (a) P + CS_2 poured upon crumpled paper on asbestos, ignites at room temperature; (b) thermometer bulb heated above 240°C. and brought to CS_2 in evaporating dish causes fire; (c) $H_2 + O_2$ mixture exposed to burner flame explodes at about 550°C.**

2-16 Iron bar, filings in shaker, burner. **Hold bar in flame, shake filings in flame, to compare rates of reaction.**

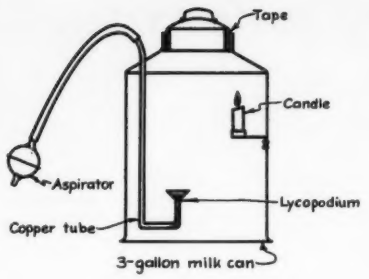


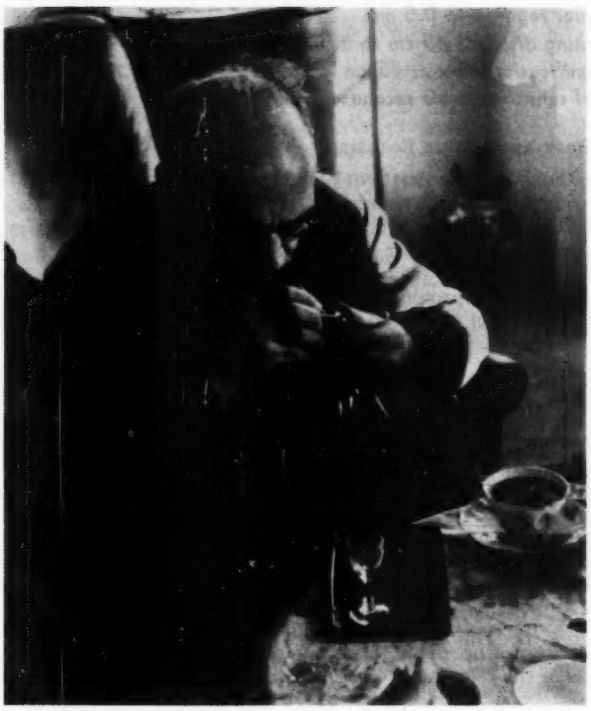
Figure 2-17

*2-17 Dust explosion can, lycopodium. **CARE: keep face away from mouth of can. Show explosion with lid off. Blow lid off.**

*2-18 Pyrophoric lead. **Demonstrate.**

Next month's Tested Demonstrations in General Chemistry

3. HYDROGEN



Heinrich Wieland

Editor's note: This picture was furnished by Dr. Hosmer W. Stone. It was taken by Bernard Witkop on the occasion of a visit by the two of them to Wieland's summer home in Starnberg, Bavaria, on January 11, 1946.

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Editor's Outlook

I HAVE repeatedly insisted that chemical education is not solely the concern of teachers, students, and other academic folk, but also of chemists in industry. In our November issue we made a special point of the contributions which academic laboratories have made to industrial developments. Now I want to supplement this with some observations of Dr. Hans T. Clarke, for a long time research chemist with the Eastman Kodak Company, although now with the College of Physicians and Surgeons of Columbia University. He says:[1]

> There is no essential difference of techniques in chemical research in industry from that in academic institutions. . . . I subscribe to the generally held opinion that the only important difference is that of motivation; the industrial research worker seeks to solve problems arising from the needs of production. . ., whereas the academic worker seeks to add to the general store of knowledge. The operational methods are much the same. . . .

This may still seem remote from chemical education. But he goes on to say:

> I should like to emphasize that a chemist engaged in industrial work has not only a golden opportunity, but an obligation, to take a hand in contributing to the advancement of his science by training the men under his care. Free of time-consuming didactic duties at elementary levels and having a relatively small number of younger men under his direction, he can guide not only their current work, but their development, more intimately than is generally possible in a university laboratory.

If we accept this (and it seems we should), then we are brothers under the skin, after all. For who can tell where a chemist will learn his trade and complete his education? When the prize is awarded and the recipient is reviewing the long course leading to the present honor, then we find out who were really his teachers, who ignited his spark of genius. It may have been a teacher in his early years or it may have been the leader of an industrial research team.

What college lecturer could have reviewed the fifty years of quantum physics more clearly and interestingly than did E. U. Condon at the last meeting of the A.A.A.S.; who could have inspired young minds more vividly than Vannevar Bush in his paper on "Science and progress" at the same meeting? Yet neither of these is associated with formal science education. Anyone working with or under such men is acquiring an education as surely as though he were registered in a graduate school.

What characteristics distinguish the successful graduate student or research worker? We all know that it is not uncommon for a brilliant undergraduate to fail when he is thrown on his own resources in the graduate school. Dr. Clarke says:

> Ability in chemical research calls for specialized, inborn talents, without which no amount of scholastic training will serve to convert a student into an investigator. . . . I wonder how widely this fact, obvious to all who have made research their principal interest, is recognized by instructors at the college level.

His analysis of these characteristics is, briefly, as follows:

(1) Infatuation with the subject. Not a guarantee of talent, it is essential for happiness and success.

(2) Ability to differentiate the most important from the less important. Though it cannot be inculcated didactically it can be fostered by competent instruction.

(3) Scientific imagination, shown by the ability to correlate diverse information in apparently unrelated areas of science.

(4) Ability to recall the essential details of experiments performed in the laboratory during training. Cannotes keenness of observation.

(5) In certain fields, such as organic chemistry, manipulative ability is also essential. Its relative measure, with scientific acumen, will determine the eventual field of greatest success.

An interesting observation which he makes concerning this last item is: "a positive correlation between the ability to secure good yields of pure products from difficult reactions and success in glassblowing." Shades of Franklin and Kraus, both of whom were masters of that art!

[1] CLARKE, HANS T., "Some experiences in the training of research chemists," *Chemist*, **31**, 353 (September, 1954).

RADIOACTIVITY AND THE AGE OF THE EARTH

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One of the most interesting applications of radioactivity has been its use as a means of determining the age of the earth. This problem has intrigued mankind throughout the centuries, and some rather curious answers have resulted. These "estimates" have varied from the seventeenth-century calculation of Archbishop Ussher that the earth was formed at 9 o'clock on the morning of October 12, 4004 B.C., to an almost equally specific date of creation arrived at by the ancient Hindus which would lead to a present age of 1,972,949,055 years. This latter value is somewhat surprising inasmuch as it is of the same order of magnitude as the most reliable estimates of the present time.

Before the discovery of radioactivity, scientific estimates of the age of the earth varied from 20 million to 90 million years. In summarizing these early estimates, Knopf (*1*) in 1931 pointed out that at the beginning of the present century the only apparent problem connected with the age of the earth seemed to be one of reconciliation of several independent estimates, all of which were of the same order of magnitude. These ranged from the 22 million years of Helmholtz, based on the source of the sun's heat, to the 90 million years of Joly, based on the rate of accumulation of sodium in the oceans, with intermediate figures such as Lord Kelvin's value of 40 million years based on the rate of cooling of the earth, and Darwin's value of 57 million years based on the separation of the moon from the earth.

These methods all suffered serious shortcomings. Any successful method of measuring geological time must fulfill three conditions: (1) it is necessary to know the rate at which a given process is going on; (2) the *total change* resulting from this process must be known for the interval of time being considered; (3) the occurrence of any variations in the rate must be known, as well as their magnitude. Obviously, without a knowledge of the contribution of radioactivity to the earth's heat, Kelvin's estimate was in error. It is also quite clear that in past geologic time the accumulation of salt in the ocean must have proceeded at different rates than at present, since geologists are convinced that during this present era the erosion of the land masses is abnormally high. Age estimates based on this method therefore necessitate certain assumptions concerning an *average* rate of buildup of salinity, some of which are of doubtful validity. Jeffreys (*2*) has also pointed out the difficulties involved in reconciling the apparently different origins and rates of accumulation of both sodium and chlorine with the fact that chlorine must have kept pace with the sodium very closely during geological time, since an excess of either would have destroyed life in the seas. Hence, such methods can at best give only orders of magnitude in age estimates, since they fail in at least one of the three conditions mentioned above.

The discovery of radioactivity with its long decay periods necessitated a radical revision of man's concept of the age of the earth. The radioactive decay chains found in nature are characterized by extremely long-lived parent isotopes which, after one or more successive nuclear transformations, produce stable isotopes, thus terminating the chain. Each such long-lived parent isotope decays exponentially with a half-life which is specific for that particular isotope. If reference is now made to the three conditions set forth above, it is apparent that, if nothing disturbs the parent-daughter relationships, any of these naturally occurring decay chains can, at least in theory, be used as a suitable clock for measuring geological time. Measurement of the decay constant of the long-lived parent fulfills the first of these conditions in that it expresses the rate at which the decay process is occurring. The second condition is met if the quantity of stable end product of the decay chain can be determined, since this is a measure of the total change resulting from the decay process. With respect to the third condition, it seems reasonably certain now that the decay rate of these long-lived radioactive isotopes has remained the same throughout geological time.[1]

It is the purpose of the present paper to examine the methods, and some of the factors which influence the results obtained, in which the phenomenon of naturally occurring radioactivity has been employed in order to arrive at estimates of the age of the earth.

UPPER LIMITS

Of the naturally occurring radioactive elements, only U^{238}, U^{235}, Th^{232}, K^{40}, and Rb^{87} have sufficiently long half-lives to be useful in age determinations.[2] It is

[1] J. Joly (*Proc. Roy. Soc.* (*London*), **A102**, 682, (1923)) from his studies on pleochroic halos in minerals, concluded that age determinations based on constancy of the radioactive decay process might be seriously in error, but later evidence refutes this view. See, for example, G. Henderson and L. Turnbull (*Proc. Roy. Soc.* (*London*), **A145**, 582, (1934)). More recently, F. Houtermans and P. Jordan (*Z. Naturforsch.*, **1**, 125, (1946)) discuss a possible variation of the rate of β-decay with time by citing abundance data on argon and its origin as an end product of K^{40} decay. But as Birch points out (*36*), the argon problem is in too uncertain a state to lend much value to the argument.

[2] Attempts have been made to use radioactive Sm^{152}, half-life 2.5×10^{11} years, for this purpose, but have not been successful due to scarcity of suitable samples; the stable Nd^{148} daughter does not occur in sufficient quantities to permit an analytical differentiation between radiogenic and nonradiogenic neodymium

comparatively easy to obtain an upper limit for the age of the earth by merely looking at the half-lives of some of these elements. From the half-life values for U^{235} (7.1×10^8 yrs.) and K^{40} (1.27×10^9 yrs.), and the fact that they still exist in appreciable quantities, it is improbable that the earth is older than 10^{10} years. Another approximation to this upper limit may be obtained by considering the U^{238} to U^{235} ratio, which at the present time is 138. Since with few exceptions odd isotopes are always less abundant than even isotopes, one can extrapolate back in time to the point when they were equally abundant, and thus obtain an upper limit of 6×10^9 years. A third approximation can be made if one makes the reasonable assumption that any system containing measurable amounts of a radioactive element cannot have been isolated longer than the time required to produce *all* of the observed stable daughter product resulting from the decay process. Thus, U^{238} by a chain of successive transformations eventually produces a stable end product, Pb^{206}. U^{235}, by a somewhat similar chain of decays, produces stable Pb^{207}. If one examines the data on the present abundances of these four isotopes, and then makes the assumption that at zero time when our system (the earth) became isolated no Pb^{207} existed, then the maximum time that system could have remained isolated comes out to be approximately 5×10^9 years. Of course, if some of the Pb^{207} is nonradiogenic in origin, the time necessary to produce the observed abundances by radioactive decay processes becomes smaller.

Calculations similar to this have been made for other radioactive series, assuming that *all* the daughter element is radiogenic in origin. Thus, if one argues that all the Ca^{40} in existence today was formed by decay of K^{40}, then taking into account their present abundances and the decay scheme and half-life of K^{40}, one obtains a value of approximately 20×10^9 years for the length of time required to form all the Ca^{40} by this method. A similar calculation can be carried out for the K^{40}-A^{40}, or the Sm^{152}-Nd^{148} decay chains, but the results in all three of these cases are subject to extremely large uncertainties (due to corresponding uncertainties in isotopic abundance values, decay schemes, half-lives, and the extent to which radioactive decay actually contributed to the observed present abundances). The value of 5×10^9 years quoted in the previous paragraph is by far the most reliable value obtained for the maximum age of the earth.

At this point it may be profitable to inquire as to just what "age" we are considering. Figures obtained in the above manner have been rather indiscriminately referred to as the "age of the elements," the "age of the universe," the "age of the earth," etc. Actually, the abundance data in most cases is based on samples taken from that portion of the earth's crust which is accessible to us for sampling. Hence, the value obtained for the upper age limit should, strictly speaking, be regarded as an estimate of the maximum time elapsed since isolation of the earth's crust. The question then arises as to the magnitude of the time interval between formation of the earth as a whole and solidification of the earth's crust. If the solar system originated in a cosmic dust cloud as centers of accumulation of matter, much of the accumulation would have an initial temperature well below the melting point. Calculations based on such an accumulation of K^{40}, uranium, and thorium from their present abundances and half-lives seem to indicate that, owing to the release of heat during the radioactive decay process, the earth would pass through a stage of liquefaction followed later by solidification of the crust. The time required for the liquefaction and subsequent solidification is estimated by cosmologists to be considerably less than 10^9 years.[3] It seems reasonable, then, to disregard the time interval which elapsed between the formation of the earth and the solidification of the earth's crust, since the magnitude of this time interval seems small compared to the age of the crust itself. Hence, in a general sense, the age of the earth's crust is usually taken (perhaps incorrectly) as synonymous with the age of the earth itself.

LOWER LIMITS

An estimate as to a lower limit for the earth's age can be made by a measurement of the age of various minerals, on the assumption that the earth must be at least as old as the rocks and minerals which form a part of its crust. Several methods based on radioactivity have been used for this purpose.

As a first approximation, a simple equation can be deduced as follows for the case of uranium decaying to lead (*3*).

If the amount of Pb^{206} produced by 1 g. of uranium in 10^6 years be $1/C$, then in t million years there will be produced t/C g. of Pb^{206}, and:

$$t = \frac{Pb^{206}}{U} \times C \text{ million years} \qquad (1)$$

In the early days of radioactivity, crude estimates of t were often obtained by straight chemical determinations of the Pb/U ratio in a given sample without attempting to take into account the possible presence of nonradiogenic lead (many minerals containing uranium, such as pitchblende, are sometimes found in close proximity to galena, a PbS ore). The contribution of Pb^{208} from any thorium which might have been in the sample was likewise neglected, as well as the decrease in the quantity of uranium itself during the lifetime of the mineral due to decay.

An approximate correction for the presence of thorium can be made by writing an expression similar to equation (1), expressing it in terms of Pb^{208} and Th.

$$t = \frac{Pb^{208}}{k \times Th} \times C \text{ million years} \qquad (2)$$

[3] See the discussion by Birch, ((*36*), pp. 120–1). Jeffreys, ((*2*), pp. 268–70), although concluding that the interval of time from liquefaction to formation of a crust may have been as short as 10^4–10^8 years, disagrees with the ideas stated above concerning the effect of radioactivity. In his opinion, the contribution of radioactivity to the earth's surface temperature, even during early history, was negligible compared to the amount of heat received from solar radiation (pp. 283–4).

where k represents the amount of uranium equivalent in lead-producing capacity to 1 g. of thorium.

In a mineral containing both uranium and thorium:

$$t = \frac{Pb^{206} + Pb^{208}}{U + k\ Th} \times C \text{ million years} \quad (3)$$

According to Holmes (*3*), acceptable values for k and C are 0.36 and 7600, respectively. Then, if one ignores the U^{235}-Pb^{207} chain, as well as any change in the amounts of U and Th due to decay during the lifetime of the mineral, the most probable expression for the age becomes:

$$\text{approximate age} = \frac{Pb}{U + 0.36\ Th} \times 7600 \text{ million years} \quad (4)$$

where Pb, U, and Th are determined chemically.[4]

TABLE 1
Age of Uraninite from Singar, Goya District, India

Chemical analysis					
Pb	*U*	*Th*	$\frac{Pb}{U + Th}$	$\frac{U}{U + Th}$	*Apparent age in millions of years*
8.92	64.3	8.12	0.123	0.89	885

Isotopic analysis of lead	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Isotopic proportions of lead (radiogenic)	—[a]	100	7.20	4.68
% of radiogenic Pb in uraninite	—	7.93	0.574	0.373
Lead ratios	207/206	$206/U^{238}$	$207/U^{235}$	208/Th
	0.0720	0.1240	0.0893	0.0459
Calculated ages (millions of yrs.)	995	883	912	1003

[a] Less than 1/20,000. Original lead is therefore negligible.

This formula, although approximate, was for a long time widely used in calculations of geological age, since it involved only straightforward chemical analysis. For more accurate results, especially for older rocks, corrections have to be introduced; Kovarik (*4*) and Keevil (*5*) have discussed in some detail methods of obtaining greater accuracy by substitution and successive approximations, including atomic-weight determinations of the lead in an effort to correct for the amount of nonradiogenic lead in the samples. However, it was not until the technique of isotopic analysis with the mass spectrometer had been perfected that the relative proportions of the lead isotopes could be determined with sufficient accuracy to allow the use of the exact equations:

$$Pb^{206} = U^{238}(e^{\lambda_{238}t} - 1) \quad (5)$$

$$Pb^{207} = U^{235}(e^{\lambda_{235}t} - 1) \quad (6)$$

$$Pb^{208} = Th\,(e^{\lambda_{Th}t} - 1) \quad (7)$$

[4] Jeffreys ((*2*), p. 261) gives slightly revised values of k and C, namely, 0.35 and 7370, respectively.

where the amounts of the above isotopes are expressed in terms of the relative numbers of atoms, and λ refers to the decay constant of the radioactive isotope concerned. Of course t refers to the age of the mineral, *i. e.*, the length of time which has elapsed since the mineral was first formed, at which instant lead began to accumulate in the mineral. If equation (6) is divided by equation (5), a fourth equation for determining t can be obtained in the form first used by Nier (*6*):

$$\frac{Pb^{207}}{Pb^{206}} = \frac{U^{235}\,(e^{\lambda_{235}t} - 1)}{U^{238}\,(e^{\lambda_{238}t} - 1)} \quad (8)$$

The amount of Pb^{204} found in the sample is taken as a measure of the amount of nonradiogenic lead. (This Pb^{204} must represent only original lead, not lead picked up by contamination; any mineral suspected of having been contaminated by lead from other sources must, of course, be discarded.)

These equations possess the advantage of giving independent age determinations on the same sample. Equation (8) possesses a distinct advantage over the others in that no accurate chemical analyses are required; it is sufficient to isolate part of the lead in a pure state and obtain the 207/206 ratio, since the present U^{235}/U^{238} ratio can be taken as 1/138. Equations (5), (6), and (7) require chemical analyses in order to determine the relative proportions of Pb, U, and Th in a given sample. In addition, to check values on the age of the mineral, the use of these equations may throw some light on the past history of the sample. For example, the 207/206 ratio is not affected by any loss or gain of Pb and/or U through leaching effects or atom exchange, whereas a loss of Pb in the past would give low results when equations (5) and (6) are used. On the other hand, loss of radon from the mineral would cause high results with equation (8), low results with equation (5), but would not affect results obtained from equation (6).

To illustrate the lead-uranium method of calculating ages, two examples will be described, one involving a uranium-rich ore containing appreciable quantities of lead and thorium, the other involving an igneous rock sample requiring the most precise methods of analysis in order to determine the microquantities of Pb and U contained therein. The first example is taken from an article by Holmes, Leland, and Nier (*7*), describing their work on a uranium-rich ore. Table 1 shows their results.

A crude age estimate calculated from equation (4) gives 1.01×10^9 years. The "apparent age estimate" in Table 1 of 0.885×10^9 is taken from a series of curves prepared by Wickman (*8*), in which the Pb/(U + Th) ratio is plotted versus the U/(U + Th) ratio for various age values, each curve showing how these ratios can vary in a mineral of a given age. (Although Wickman's formula on which these curves are based is considered to be somewhat more exact than the older and more widely known equation (4), it is still only an approximation, since it relies on chemical analysis only,

with an assumed average atomic weight of 207 for radiogenic lead.) The Pb^{207}/Pb^{206} ratio according to equation (8) gives 0.995×10^9 years. The Pb^{206}/U^{238} ratio gives the value 0.883×10^9 years according to equation (5), the Pb^{207}/U^{235} ratio gives 0.912×10^9 years from equation (6), and the Pb^{208}/Th ratio gives 1.003×10^9 years according to equation (7). The question is, which result is more nearly correct? This decision is usually based on geological considerations, such as the condition of the rock sample and its environment. The authors in their article discuss in some detail the possible reasons for these variations in age. From the physical condition of the sample, which, though free from any visible alteration products, was penetrated through by clean cracks, they concluded that loss of radon was the most probable cause. If loss of radon were the only cause, the Pb^{207}/U^{235} ratio would have remained unchanged, and the figure of 0.912×10^9 years would be most nearly correct. But certainly other effects occurred, such as loss or gain (leaching, atom exchange, etc.) of Pb, U, and/or Th; such effects would leave the 207/206 ratio unchanged, and the figure of 0.995×10^9 years would be most probable. Since there is no way of determining how each of these elements has behaved in the past, "the evidence remains insufficient to yield an unambiguous solution" (*7*). The conclusion is therefore reached that the age of this particular mineral is less than 0.995 but more than 0.912×10^9 years, the most probable figure being $(0.995 \pm 0.040) \times 10^9$ years.

The second example is illustrative of what can be done even when extremely low concentrations of lead and uranium are involved. Tilton, Patterson, Brown, Inghram, Hayden, Hess, and Larsen (*9*), by a combination of isotopic dilution analysis and mass spectrometer determinations of isotopic ratios, were able to calculate the ages of mineral inclusions within a granite rock sample by determining the Pb^{207}/Pb^{206}, Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{208}/Th^{232} ratios. A brief description of a selected portion of their work is as follows. Samples of a zircon mineral which had first been isolated from the rock were dissolved by a borax fusion–HCl treatment. Aliquots were then "spiked" with known amounts of lead enriched in Pb^{208}, and uranium enriched in U^{235}. Chemical separation of the lead was accomplished by chloroform extraction of lead dithiozonate; uranium was separated by extraction of the nitrate into methyl isobutyl ketone. After separation and purification, the isolated lead and uranium samples were subjected to mass spectrometer isotopic analysis. These procedures, which involved microgram quantities of the elements concerned, required the most stringent precautions to avoid contamination from the atmosphere, the reagents, and the apparatus (*9*). Table 2 shows the composition of the zircon and the ages calculated according to the above ratios.

The amount of nonradiogenic lead was taken as zero, since the amount of Pb^{204} in the zircon lead was found to be negligible. The ages shown were calculated according to equations (5), (6), (7), and (8). The disagreement between the Pb^{208}/Th^{232} age and the others is obvious. The reason for this discrepancy must be due either to (*a*) addition of thorium without any change in the uranium content, or (*b*) loss of Pb^{208} without any change in the Pb^{206} or Pb^{207}. The authors (*9*) discuss the problem in detail, and indicate

TABLE 2
Isotopic Composition of Lead and Ages of Zircon from Essonville, Ontario, Canada

Pb^{204} (μg./g.)		0.00
Pb^{206} (μg./g.)		392 ± 10
Pb^{207} (μg./g.)		29.5 ± 7
Pb^{208} (μg./g.)		38.4 ± 1
Total U (μg./g.)		2650 ± 40
Total Th (μg./g.)		2180 ± 20
Age in millions of yrs.	207/206	1060
	$206/U^{238}$	1020
	$207/U^{235}$	1050
	$208/Th^{232}$	390

that the probable reason has been selective loss of Pb^{208}. With the procedure which they used, in which isotope dilution analysis is used in conjunction with a mass spectrometer, it is possible to carry out age determinations on samples which previously could not be used because of their low lead and uranium concentrations and the difficulties involved in both chemical and isotopic analyses.

These figures have been quoted in some detail to illustrate the results which may be expected when age measurements are based on careful chemical and isotopic analyses. Probably the oldest dated minerals measured thus far by the "lead clock" method have come from Southern Rhodesia, Africa. Holmes (*10*) has calculated an age of 2600 million years for a sample of monazite from this region, and has obtained excellent agreement among the four ages calculated according to equations (5), (6), (7), and (8). Since this mineral occurs in a pegmatite which cuts much older rock formations, it must be concluded that the minimum age of the earth's crust according to the "lead clock" method is closed to 3×10^9 years.

A second method, similar in principle to the one just described, is the "helium clock" method. In the chain of successive decays in going from uranium and thorium to lead, alpha particles (helium nuclei) are produced. Since these alpha particles have a very short range in such comparatively dense substances as rocks, most of these helium atoms remain entrapped therein. An expression similar to equation (4) above can be derived (*3*) in the same manner for a mineral containing both uranium and thorium.

$$\text{Approximate age} = \frac{\text{He}}{\text{U} + 0.27\ \text{Th}} \times 8.8 \text{ million years} \quad (9)$$

where the He is expressed in cc. per 100 g. of sample, and U and Th are determined chemically. (One hundred g. of pure uranium, for example, produces

about 1.2×10^{-5} cc. He per year.) Obviously, this method suffers from a serious shortcoming owing to the fact that the helium does not in many cases remain quantitatively entrapped, even for very impervious fine-grained rocks; also, in preparing the sample for analysis, such treatment as grinding, dissolution in acid, etc., may cause loss of entrapped helium. Low results in the past when using the helium method have been attributed to these factors. Recently, however, Hurley (*11*) seems to have found evidence that these low results have been caused, not by loss of entrapped helium from the interior of the rock, but rather by an excess of (U + Th) on the surfaces of the individual mineral grains. He advanced the tentative explanation that some rocks can absorb excess amounts of these elements on crystal surfaces, grain boundaries, etc., where the helium they generate can easily leak out. When this excess (U + Th) is removed by acid washes, the original (U + Th + He) remains, and the age determinations fall more in line with the Pb time scale. These results are as yet preliminary, and whether the past discrepancy between "helium clock" and "lead clock" ages will disappear remains to be seen.

Age measurements on the oldest rocks found thus far have been made by a method identical in principle to those described above, but different in detail in that it is based on the decay of rubidium to strontium (*12*). Rubidium as found in nature consists of two isotopes, Rb^{87} (27 per cent abundant) and Rb^{85} (73 per cent abundant). The former of these two isotopes is radioactive, decaying by beta emission to inactive Sr^{87}, the half-life for this process being 5.8×10^{10} years. Since this is long compared to geologic time, only an insignificant portion of the Rb^{87} will have decayed since formation of the earth's crust, and consequently one may regard the quantity of Rb in a given mineral or rock sample as having remained constant. The usual expression for radioactive decay:

$$N = N_0 e^{-\lambda t}$$

can then be simplified to:

$$N_0 - N = \lambda t N$$

where $N_0 - N$ = number of Rb atoms decayed, and $\lambda t N$ = number of Sr atoms formed. That is,

$$Sr^{87}\text{ (radiogenic)} = Rb^{87} \times t \times \lambda$$

or

$$t = \frac{Sr^{87}}{Rb^{87}} \times \frac{1}{\lambda} \qquad (10)$$

This is an approximation, of course, but for values of t up to about 3×10^9 years the error amounts to only about 3 per cent or less, much better than the actual analytical data obtained on the rocks or minerals, or indeed the precision of λ itself which in this case is only $\pm$ 10 per cent.

Analysis of suitable rock samples for rubidium and strontium presents some formidable problems. Since the amount of Rb in rocks and minerals is itself quite small (the highest percentage being found in lepidolite which contains about 1.5 per cent Rb), the quantity of radiogenic strontium found therein will be smaller by several orders of magnitude. The usefulness of this method depends, therefore, on the accuracy with which quantities of Rb as low as 0.05 per cent, and of Sr as low as 0.02–0.0002 per cent can be quantitatively determined. For these small quantities, the best analytical method found thus far has been spectroscopic analysis, where the Rb/Sr ratio can be determined on a single sample by the intensity ratios of a pair of Sr and Rb lines. Ahrens, who has been the only worker in this country to have used this method extensively, has determined the ages of some thirty or so rock specimens from their Rb/Sr ratio; the oldest of these (*13*) lies between 2.1 and 2.4×10^9 years.

An important question in the Rb-Sr clock method is the relative amount of common Sr found in the sample, as distinct from radiogenic Sr formed by Rb^{87} decay. If the former predominates over the latter, the spectroscopic Rb/Sr ratio when used in equation (10) will lead to erroneous results. Fortunately, in samples of lepidolite it turns out that about 99 per cent of the Sr found therein is radiogenic, and no error is incurred in using the spectroscopically obtained Rb/Sr ratio. In other types of minerals the situation is not so fortunate; in most cases common Sr predominates by far over radiogenic Sr, and if age determinations are to be carried out, isotopic analyses become necessary. This is extremely difficult when the sample contains small quantities of Sr. Davis and Aldrich (*14*) have attempted this by an isotope dilution method of analysis, in which strontium of abnormal isotopic composition was used for "spiking" rock samples, followed by mass spectrograph determinations of the Sr 88/84 and 87/84 ratios. These ratios were taken as a measure of common Sr and radiogenic Sr, respectively. The claim is made that age determinations by this method can be made on minerals such as the biotites and feldspars, in which the ratio of common to radiogenic Sr may be as high as 20.

Tomlinson and Das Gupta (*15*) have also determined the amount of radiogenic Sr by the isotope dilution technique, using fission product Sr^{90} to spike their samples. The method is claimed to be successful even for samples as small as 100 mg. of mineral with a total Rb content of the order of 0.01 per cent. (This would mean a total Sr content of about 0.0001 per cent, with an unknown fraction of common Sr to be determined by isotopic analysis.)

The results obtained in both cases where isotope dilution was used seem high. Davis and Aldrich report ages as high as 3.1 and 3.4×10^9 years on certain lepidolites, substantially higher than previous determinations. Tomlinson and Das Gupta report an age of about 3.4×10^9 years on a sample of biotite from Saskatchewan, whereas the age of a uraninite mineral with which it was found was determined to be $1.9 \times$

10^9 years by the lead isotope method. But another sample of biotite from New Hampshire showed an age of 0.57×10^9 years when measured by the Rb-Sr method, in reasonable agreement with ages of lead minerals in the same area of 0.40×10^9 years as measured by the lead isotopic method. Clearly, unknown forces acting on these rocks in past times may be responsible for such results; for example, the uraninite age determinations may be somewhat in error due to loss of radon (one of the intermediate products in the U^{238}-Pb^{206} chain) from the rocks. Which figures are more correct remains to be seen.

In all of the above methods for determining the ages of rocks and minerals, a basic assumption has been that the only major changes taking place throughout geologic time have resulted from radioactive decay. Any outside influences which may cause changes in the parent-daughter relationships in the decay chains considered (such as mixing with or contamination by other ores during orogenic processes, selective leaching effects, loss of randon, etc.) will, of course, cause error. Selection of suitable samples on the basis of their past geologic history is therefore of prime importance; not just any rock or mineral will do. This will be considered in a little more detail further on.

Before concluding this discussion on the measurement of the age of minerals, brief mention should be made of the subject of pleochroic halos and age determinations. It is well known that some types of radiation can cause coloration effects in many materials. The coloration of glass containers when inserted into a nuclear reactor is a good example of this. Likewise, small quantities of uranium, thorium, or other alpha sources can produce noticeable effects over extremely long periods of time. In natural materials, such as biotite or fluorspar, this is manifested by a series of very small concentric rings surrounding the natural alpha emitter at the center. These rings are called pleochroic halos, since under polarized light they exhibit various colors. Their origin was a mystery for many years, until 1907 when Rutherford produced the same phenomena in the laboratory from known alpha sources. The differing radii of the rings correspond to the different alpha particle ranges of the members of the uranium or thorium families; the formation of the rings at definite distances from the source is caused by the fact that the ionizing effect of an alpha particle is greatest just before it comes to rest.

Many of the great pioneer names in the field of radioactivity devoted much time and effort to trying to correlate these rings with the age of the mineral in which they were found, by exposing the mineral to known amounts of alpha radiation to give measurable degrees of blackening. By comparison with natural halos in the same mineral, the number of alpha disintegrations required to give rise to the naturally occurring pleochroic halos could be estimated; from this, of course, the number of uranium atoms which had decayed, and the time required for this decay (based on the amount of uranium existent at present in the mineral) could be estimated. In this way, ages of minerals have been obtained that range from 20 to 2400 million years. However, bleaching effects due to overexposure, the difficulty of measuring the extremely small quantities of radioactivity at the center of a particular set of halos, and other limitations made it almost impossible to get accurate results. The method is no longer of widespread use, and is regarded today as being chiefly of historical interest ((*3*) part IV, chap. 2.)

THE AGE OF THE EARTH'S CRUST

The methods described above have enabled us to establish to a fair degree of approximation a maximum and a minimum age of the earth, namely, about 5×10^9 years and 3×10^9 years, respectively. It was not until 1946 that a new approach was made to the problem which, in addition to fixing upper and lower limits, promised for the first time to give a possible answer as to the actual age of the earth's crust. Holmes (*16*, *17*) in Scotland, and independently of him, Houtermans (*18*) in Germany, first worked out the method, which is based on variations in the isotopic constitutions of lead ores formed at different times in the earth's history, these variations having resulted from addition, in varying amounts, of radiogenic lead to primeval lead. All calculations were based on mass spectrograph isotopic analyses carried out by Nier and his collaborators (*19*, *20*) on 25 carefully selected lead ores from all over the world. Because of the inherent interest of the method, it may prove instructive to examine it in some detail, without, however, attempting to go through the rather complex numerical calculations involved.

Lead as found in nature consists of four stable isotopes of masses 204, 206, 207, and 208. Of these, only the nonradiogenic Pb^{204} has remained unchanged in abundance throughout the earth's history, and therefore can be taken as a measure of the quantity of original lead. Pb^{206}, Pb^{207}, and Pb^{208} are the end products of the radioactive decay chains starting with U^{238}, U^{235}, and Th^{232}, respectively; they are therefore found in varying abundances. Initially (and this would probably be true regardless of whether the initial stages of the earth's formation involved gases, liquids, or clouds of dust particles), Holmes assumed that the original quantities of the four lead isotopes first formed during the birth of the elements were mixed so thoroughly that they existed in the same relative proportions everywhere throughout the earth. This mixing process probably continued up to the time of formation of a solid crust, since it is improbable that a given lead ore with a specific isotopic composition could have been preserved except in the solid state. When the crust solidified, therefore, the initial isotopic composition of all lead therein represented the original proportions of the lead isotopes in addition to that contributed by radioactive decay of uranium and thorium up to the time of crust formation. (If this latter interval is presumed to be small, as previously pointed out, then

the age of the earth's crust becomes approximately the same as the age of the earth.) This lead which was present in the crust at the time of its solidification was called "primeval lead" by Holmes. Now during the process of solidification of the crust (a very short time, geologically speaking) differences in the chemical behavior of uranium, thorium, and lead (during such phenomena, for example, as recrystallization processes) produced an unequal distribution of the three elements throughout the crust (*2*). Thereafter, continued decay of uranium and thorium began to produce variations in the isotopic composition of lead in different places, the extent of the variations being dependent on the relative proportions of uranium, thorium, and lead at the different locations. At some later time a lead ore was isolated from the surrounding rock magma; since this isolated lead ore was now permanently separated from contact with the uranium and thorium in the rock, it remained unchanged and provides us now with a record of the isotopic composition of lead at the time of its isolation.

A mathematical expression can now be set up in conformance with the above situation. Let t_0 represent zero time, the time when uranium and thorium began decaying to produce lead—or rather, the time of solidification of the earth's crust, since differences in isotopic distribution would be unlikely to exist in any gaseous or liquid stage which may have preceded solidification. Let t represent the time of separation of the lead ore from the rock magma containing its parent elements, there then being no further changes in the isotopic constitution of the lead from time t to the present. That is to say, from t_0 to t a certain amount of U^{238} decayed to Pb^{206} (and U^{235} to Pb^{207}). At time t, the lead ore became separated from its parent, and further production of radiogenic lead *in the ore* ceased. It is apparent that in the lead ores more recently formed the amount of radiogenic lead found therein will be higher than in old lead ores. It is possible, then, to set up two material balance equations[5] based on the exponential radioactive decay law:

$$X = X_0 + A(e^{\lambda_A t_0} - e^{\lambda_A t}) \qquad (11)$$

$$Y = Y_0 + B(e^{\lambda_B t_0} - e^{\lambda_B t}) \qquad (12)$$

where X and Y are the observed present-day abundances of Pb^{206} and Pb^{207}, respectively, expressed relative to nonradiogenic Pb^{204} taken as unity; X_0 and Y_0 represent the initial amounts of Pb^{206} and Pb^{207} present in primeval lead at time t_0; A and B are the number of atoms of U^{238} and U^{235}, respectively, which are present in the source magma at the present time; λ_A and λ_B are the decay constants of U^{238} and U^{235}. These equations simply state that the amount of lead isotope found now in the lead ore is equal to the amount present in primeval lead plus the amount subsequently formed by radioactive decay during the interval t_0 to t. Fortunately, since the present-day ratio of U^{238} to U^{235} in nature is found to be 138, regardless of the source, one can eliminate the necessity for tedious chemical analyses for small quantities of uranium by transposing and dividing (11) by (12). This gives:

$$\frac{X - X_0}{Y - Y_0} = \frac{138\ (e^{\lambda_A t_0} - e^{\lambda_A t})}{(e^{\lambda_B t_0} - e^{\lambda_B t})} \qquad (13)$$

The values for X and Y are based on the isotopic analyses performed by Nier. Values for t, the age of the lead ore, are usually obtained from geologic, or stratigraphic data; in some cases the lead ores may also be dated by age measurements on uranium minerals which occur in the same geological formations.

This now leaves us with three unknowns, X_0, Y_0, and t_0, the latter of which we wish to know. By appropriate mathematical methods, these unknown parameters are chosen so that equation (13) above makes the best fit with the experimental data of Nier on the isotopic composition of lead ores of known ages. Holmes (*17*) originally used a rather laborious graphical method to calculate t_0; his value of 3.35×10^9 years has been criticized by Jeffreys (*21*) and McCrady (*22*) with respect to its statistical validity. By a least squares method, Bullard and Stanley (*23*) obtained a value of 3.29×10^9 years, also using the set of Nier data. More recently, Collins, Russell, and Farquhar (*24*) made isotopic analyses on several new samples of lead ore; using these in addition to the Nier data, they calculated a value of 3.5×10^9 years for t_0, also by a least squares method.

These three results, by different investigators using different methods of calculation (and in the last case mentioned above with additional experimental data), suggest that answers differing appreciably from 3.4×10^9 years are not likely to be obtained when using equation (13) as long as the fundamental assumptions of Holmes are considered justified. His first assumption, that at the time of solidification of the earth's crust all lead within the crust possessed a uniform isotopic composition, has already been mentioned. Holmes made a second assumption which has been severely criticized in some quarters. This second assumption was that the amounts of uranium, thorium, and lead relative to each other have remained unchanged throughout the earth's crust *except* for the changes produced by radioactive decay. This assumption is made necessary by our ignorance concerning the geologic history of the samples of lead ore used; otherwise, a detailed knowledge of any changes in the lead isotopic ratios by processes other than radioactive decay would be necessary for each sample. This would include, for example, such changes as those associated with further orogenic processes in the earth's crust (sedimentation, leaching, weathering, recrystallization, mixing of two or more different ores by upheavals, etc.). However, Holmes presents convincing arguments for justifying this assumption; briefly summarized, they are that from a geological standpoint any multiple orogenic processes in the histories of the Nier samples *probably* involved only small changes in the U/Pb ratios. Furthermore, any increases or decreases in such ratios

[5] A third equation based on Th^{232} decay to Pb^{208} should also be included, but has been omitted here for the sake of brevity.

probably occurred with equal probability over long periods; the main trend of radiogenic deposition of Pb may then be supposed to be approximately that which *would* have occurred had there been *no* orogenic processes. The validity of such an assumption is perhaps questionable; indeed, samples of lead have been reported whose isotopic composition seems to indicate that there are exceptions to the rule. However, it seems to this author that, in view of our lack of detailed knowledge concerning the past histories of any lead-ore samples, this assumption must be made.

Mention should be made at this point of the further use of equation (13) to obtain a maximum age of the earth's crust. McCrady (*22*) and Alpher and Herman (*25*) have calculated this upper limit to t_0 by assuming that at t_0 one of the primeval lead isotopes had zero abundance. McCrady, by assuming that $Pb^{207} = 0$ at $t_0 = 0$, obtained a value for t_0 (max.) of 5.1×10^9 years. Alpher and Herman, by assuming that $Pb^{206} = 0$ at $t_0 = 0$, obtained a value of 5.3×10^9 years. Following McCrady's argument, this would mean that if the earth existed *before* this time, either there was no U^{235} to produce Pb^{207} (which is improbable, as the amount of radioactive parent increases as we go back in time), or else some process selectively destroyed all the Pb^{207} produced prior to that time, which is unlikely. It is, however, improbable that no Pb^{207} was formed to begin with, since the theory of formation of the elements accounts for the origin of the heavy elements from lighter ones by means of successive neutron captures. Thus, there would seem to be no way to form Pb^{208} without passing through either Pb^{207} or Th^{207} (which latter would in turn decay to Pb^{207}). Hence, the origin of matter should come *after* a point in time 5×10^9 years ago.

COMPARISON OF TERRESTRIAL LEAD ISOTOPIC RATIOS WITH METEORITIC RATIOS

The most recent estimate of the age of the earth has been based on a comparison of isotopic lead ratios in meteorites with terrestrial lead ratios. Two assumptions are made here: first, that the only changes in terrestrial Pb/U ratios were a result of radioactive decay; second, that since in certain meteorites the amount of uranium present is quite small compared to the lead content, the isotopic composition of the lead in these particular meteorites is essentially the same as the isotopic lead composition which existed in the earth at the time of its formation. The isotopic lead composition of one of these low-uranium meteorites has recently been accurately determined by Patterson, Brown, Tilton, and Inghram (*26*); the isotopic ratios were 1/9.41/10.27 for Pb^{204}, Pb^{206}, and Pb^{207}, respectively. (The uranium content of this meteorite was 0.009 p. p. m., as compared to a lead content of 18 p. p. m.) Present values for terrestrial isotopic lead ratios can be obtained from Nier's data on the 25 lead-ore samples mentioned previously; since Nier's values represented the ratios at various times t (time of separation of the ores), a present value can be obtained for any particular ore by use of the usual exponential equation:

$$X = x - U^{238}(e^{\lambda_{238}t} - 1) \tag{14}$$

where $X = Pb^{206}$ at time t (Nier's data), x = contemporary Pb^{206} (if radiogenic production of Pb in the lead ore had not ceased at time t), $U^{238} = U^{238}$ at the present time, and λ_{238} = decay constant of U^{238}. A similar equation applies for Pb^{207} and U^{235}. Collins *et al.* (*24*) have done this by a process involving averaging all 25 ore samples; they obtain for the contemporary lead isotopic ratios 1/18.45/15.61 for Pb^{204}, Pb^{206}, and Pb^{207}, which may be considered as typical of the *average* values which *would* exist today had the buildup of Pb^{206} and Pb^{207} gone on uninterrupted in the lead ores from time t to now. In other words, these values may be taken as representative of the average abundances of the lead isotopes in the earth's crust at the present time.[6] It is now possible to calculate the length of time T required for Pb^{206} and Pb^{207} to increase from their meteoritic or original abundance values to their contemporary terrestrial values by radioactive decay, according to the following equations:

$$(x - X_0) = U^{238}(e^{\lambda_{238}T} - 1) \tag{15}$$

$$(y - Y_0) = U^{235}(e^{\lambda_{235}T} - 1) \tag{16}$$

Dividing (15) by (16), we obtain

$$\frac{(x - X_0)}{(y - Y_0)} = \frac{U^{238}(e^{\lambda_{238}T} - 1)}{U^{235}(e^{\lambda_{235}T} - 1)} \tag{17}$$

Substituting the following numbers in equation (17),

x = contemporary $Pb^{206} = 18.45$
y = contemporary $Pb^{207} = 15.61$
X_0 = meteoritic $Pb^{206} = 9.14$
Y_0 = meteoritic $Pb^{207} = 10.27$
U^{238}/U^{235} = present day $U_{238}/U_{235} = 138$
$\lambda_{238} = 1.536 \times 10^{-10}$ years^{-1}
$\lambda_{235} = 9.802 \times 10^{-10}$ years^{-1}

we obtain

$$.01227(e^{9.802 \times 10^{-10}T} - 1) - (e^{1.536 \times 10^{-10}T} - 1) = 0$$

from which T can be found by either a graphical or a substitution method, the correct value of T being that for which the above function of T becomes equal to zero. Solving, $T = 4.5 \times 10^9$ years.[7]

In a similar manner, one can use values for the present lead isotopic ratios found in samples from the

[6] McCrady (*22*) has calculated contemporary ratios of 1/23.02/16.17 for Pb^{204}, Pb^{206}, and Pb^{207}, which differ slightly from Collins *et al.* The reason for this lies in the values of t used in the calculations—*i. e.*, the method of dating the lead ore. McCrady arranged the ores chronologically and obtained his values for t from relative isotopic abundance versus time curves, on the assumption that the oldest ores contained the least amount of radiogenic lead, and vice versa. Collins *et al.* used a combination of geologic dating and age determinations on uranium-containing rocks found in the same rock strata as the lead ores to determine their values of t. Without attempting to determine which method gives the better results, the author of this article will use the value obtained by Collins *et al.*

[7] Using McCrady's values for contemporary Pb ratios, $T = 4.0 \times 10^9$ years.

Pacific Ocean. Patterson (*27*) has reported these values to be 1/18.93/15.73 for Pb^{204}, Pb^{206}, and Pb^{207}, respectively.[8] Using these values for x and y in equation (14) above, T is calculated to be 4.5×10^9 years.

The assumption involved in this method of calculation, that the earth and the meteorites were formed at the same time, naturally raises the question as to whether age determinations can be carried out on the meteorites themselves. Paneth and co-workers (*28*) have made a number of such age determinations, and have obtained values ranging from 0.06×10^9 to 7.6×10^9 years. These determinations were based on the helium content of the meteoritic samples, and necessarily involved the assumption that the He was of radiogenic origin. Two explanations have since been advanced to explain the wide range of values obtained: (1) production of nonradiogenic helium by cosmic-ray bombardment, resulting in high values, and (2) helium loss at high temperatures, perhaps caused by passage close to the sun, resulting in low values. As yet the question has not been satisfactorily resolved.

The ages of two stony-type meteorites have been measured recently by Gerling and Pavlova (*29*). This was based on the K^{40}-A^{40} decay chain, and required analysis of the two samples for potassium and argon contents. It was assumed that (1) all the argon was radiogenic, and (2) no argon was lost from the silicate structure of the meteorite. The two age values were calculated to be 3.03×10^9 and 3.00×10^9 years, which are certainly in good agreement with Holmes' value for the age of the earth's crust. There is a question, however, as to the validity of the two assumptions made in obtaining these values. An isotopic analysis of the argon, if it could be carried out, would definitely settle any question as to the first assumption. A feasible method of settling the question as to retention of the argon in the interior of the sample has not yet been suggested. If loss had occurred, however, the calculated age would be low; assuming that the amount of nonradiogenic argon is negligible, the above value of 3×10^9 years would then represent a minimum value for the age of the meteorites.

[8] These values obtained from ocean samples agree closely with the values of Collins *et al.*, obtained from lead ores. McCrady's values are not in such good agreement.

TABLE 3
Isotopic Abundances of Lead

Sample	*Isotopic abundances relative to Pb^{204} = 1.00*		*Reference*
	206	207	
Arizona, U. S. A. (age 2.5×10^7 yrs.)	18.8	15.85	(*24*)
Ontario, Canada (age 2.5×10^9 yrs.)	14.05	14.92	(*24*)
Rosetta Mine, S. Africa (age unknown)	12.65	14.27	(*24*)
Primeval lead (calculated)	10.95	13.51	(*17*)
Primeval lead (calculated)	11.86	13.86	(*23*)
Primeval lead (calculated)	11.33	13.55	(*24*)
Original lead (meteoritic)	9.14	10.27	(*26*)

It will be recalled that equation (13) contains three unknowns, X_0, Y_0, and t_0, these quantities representing Pb^{206} primeval abundance, Pb^{207} primeval abundance, and the age of the earth's crust, respectively. In determining t_0, X_0 and Y_0 are necessarily determined also, since the method of solution consists of assigning such values to these three parameters as to make equation (13) best fit the experimental data on the isotopic composition of the lead-ore samples. It may be instructive to compare the values of X_0 and Y_0 obtained by different investigators with those values found in low-uranium type meteorites, which are taken to be representative of original lead (see Table 3). For further comparison there is included the isotopic composition of a lead from the Rosetta Mine in South Africa, determined by Collins *et al.* (*24*), who list its age as being unknown. The oldest known lead ore, as well as a comparatively young sample (ages determined geologically), are also included.

Since the oldest lead ores contain the least amount of radiogenic lead, all ores isolated after the solidification of the earth's crust should have greater abundances than primeval lead. This is indeed so; no lead sample yet found has isotopic abundances less than primeval lead. However, there is a decided difference between the primeval lead values as calculated from equation (13) and those found in the low-uranium type meteorites. This may be because of an error in the basic assumptions made by Holmes in setting up equation (13) (*e. g.*, the assumption that radioactive decay alone was responsible for changes in the relative amounts of uranium and lead, and that this process proceeded undisturbed from time t_0 to time t, after which the isolated lead ore remained unchanged in composition), or it may possibly be due to an actual difference in age between the meteorites and the earth's crust at the time of its solidification. It has been assumed that this time interval between formation of the earth and solidification of its crust is quite small. But if 4.5×10^9 years represents the age of the earth, and 3.4×10^9 years be taken as the age of the earth's crust, then the difference of 1.1×10^9 years should represent the interval of time between formation of the earth and solidification of its crust. This is not negligibly small compared to the age of the crust.

There have been some attempts made to estimate the magnitude of this interval. As mentioned previously, Jeffreys ((*2*), pp. 268–70) has estimated the time required for solidification of the crust to be from 10^4 to 10^6 years. Voitkevich (*30*), in calculating the age of the earth's crust to be 3.3×10^9 years, makes the estimate that the interval between liquefaction and the first formation of a solid crust could have been as short as 20,000 years. Rostagni (*31*) has made some calculations based on abundances and decay of K^{40} into A^{40}, and has arrived at the conclusion that the earth must have been in a fluid state for at least 10^9 years. His calculations were based partly on the assumption that accumulation of A^{40} in the atmosphere ceased after solidification of the crust. Tatel (*32*)

has carried out a similar calculation, and concluded that if there were no escape of argon from the earth's interior after crystal formation, then the earth must have existed at least 5×10^8 years prior to that time. However, a large element of uncertainty is associated with these figures, since it is not known just how much argon has remained entrapped within the earth since solidification of the crust. Katcoff, Schaeffer, and Hastings (*33*) made an estimate as to the period of time between formation of the elements and formation of the earth's atmosphere, based on decay of I^{129} to form the Xe^{129} found at the present time in the atmosphere; the original abundance of I^{129} was assumed to have been equal to the present abundance of I^{127}. This interval of time was calculated to have been 2.7×10^8 years, equivalent to about 15 half-lives of I^{129}. It does not necessarily disagree with Rostagni's figure; if the latter were true, it would simply mean that all but a negligible portion of I^{129} decayed while the earth was still in a liquid state.

At any rate, it is difficult to make a comparison with the 1.1×10^9 years interval mentioned above; in view of the assumptions which must be made concerning the very early stages of the earth's history, it is not clear that all these figures represent the same period of time. The total interval between formation of the earth and formation of a crust may possibly be subdivided into two periods: the time required to melt the interior by radioactive heating, followed by the time interval required for solidification of the crust.

RADIOACTIVITY OF K^{40}

K^{40} may decay in either of two ways: by β-emission to form Ca^{40}, or by K-capture to form A^{40}. The total decay constant λ is therefore the sum of two partial decay constants λ_K and λ_β. The half-life of K^{40} is then $0.693/\lambda$. Several investigators in the past have attempted to use "partial" half-lives, based on the two alternative decay processes, but this is misleading and should be discontinued. The decay scheme of K^{40} has undergone some rather widespread fluctuations in recent years; for example, the branching ratio $(\lambda_K/\lambda_\beta)$ in 1947 was reported as high as 1.9, and in 1950 as low as 0.05. This branching ratio, which determines the value of λ, is of primary importance when K^{40} and its decay products are used in age calculations. Up to the present time, the most reliable work on the complete decay scheme of K^{40} seems to be that of Sawyer and Wiedenbeck (*34*). They report a value of 28.3 for the β's/sec./g. of ordinary potassium, and a value for the branching ratio of 0.13; this gives for λ a value of 5.48×10^{-10} yr.$^{-1}$, and a half-life of 1.27×10^9 years.

Measurements of the age of minerals from the K^{40}/Ca^{40} ratio are difficult to carry out, since a correction must be made for the amount of nonradiogenic Ca^{40}. This has been successfully accomplished in a few instances (*35*), but involves a combination of isotope dilution and mass spectrometer isotopic analyses, both highly specialized techniques. The ratio can, however, be used to set a maximum age; as mentioned previously, this is calculated to be about 20×10^9 years with respect to the age of the earth, on the assumption that all terrestrial Ca^{40} is of radiogenic origin. So far, at least, no inconsistencies have arisen from using the ratio in this manner; *i. e.*, maximum ages from the K^{40}/Ca^{40} ratio have always been greater than ages calculated by more exact methods.

The A^{40}/K^{40} ratio has also been used to determine the ages of rocks, according to equation (18).

$$A^{40}/K^{40} = \frac{\lambda_K}{\lambda_K + \lambda_\beta}(e^{\lambda t} - 1) \qquad (18)$$

Here, as in the case of the helium clock method, possible leakage of argon from the rock is important. The amount of nonradiogenic argon should also be determined; as in the case of the Ca^{40}, this has been done by the combination of isotope dilution analysis and mass spectrometer isotopic analysis (*35*).

The use of K^{40}-A^{40} abundances in attempts to determine the age of the earth is intimately related to the question of the escape of argon from the earth's interior. Birch (*36*) has discussed in detail the complicated problem of the amount of argon in the atmosphere, the terrestrial abundance of potassium, and a postulated rate of escape of argon from within the earth. Tatel (*32*) has concluded that the potassium in the crust can account for less than one-tenth of the argon in the atmosphere. By using meteoritic data to estimate the abundance of potassium in the earth's mantle (the layer immediately below the crust, extending to the earth's core, comprising two-thirds of the mass of the earth as compared to less than one per cent represented by the crust), Tatel concluded that there is enough potassium in the earth to have produced all the argon in the atmosphere in 1.5×10^9 years.

Chackett (*37*) has attempted to calculate the age of the atmosphere from abundance data on atmospheric argon and terrestrial potassium. He assumed that the argon was generated from a time t_0 to a time t when the earth's crust first began to solidify, and then equated the amount of K^{40} which had decayed during this interval to the amount of argon observed in the atmosphere. By assuming $t = 2 \times 10^9$ years ago, a value of 3.5×10^9 years was obtained for t_0. But there is no valid reason, so far as the author of this paper can see, for assuming such a value for t, when the lead method seems to have so well established this time as being close to 3.4×10^9 years ago. In further comparing his value of t_0 with the figure of 3.4×10^9 years, Chackett has overlooked the fact that the lead method of Holmes actually refers to the age of the earth's crust, not the age of the earth, and is therefore equivalent to his time t, rather than t_0.

Using a similar method of calculation, and substituting for t the value 3.4×10^9 years (the time when the crust solidified to such an extent that mixing of lead isotopes ceased and radiogenic argon no longer escaped to the atmosphere), the present author obtains

for t_0 a value close to 4.2×10^9 years ago. This agrees with the most recent value for the age of the earth, 4.5×10^9 years, as calculated from a comparison of meteoritic and terrestrial lead abundances (see Part IV of this article).

SUMMARY

It may be instructive to compare the results obtained by the several methods involving radioactivity, and to include for further comparison age estimates made by other methods (*38*). Table 4 shows these results.

It is really remarkable that such a variety of methods should give results which agree so well in order of magnitude. As pointed out by Chandrasekhar (*39*), this time scale throughout the universe of the order of a few billion years does not seem to be accidental. Such a time scale seems to lead back to some common starting point for all these processes. It seems unlikely at the present time that any values radically different from those already quoted for the age of the earth will be found; efforts in the future will most likely be devoted to narrowing the interval between the minimum and maximum estimates by accumulation of additional analytical data and refinement of the statistical methods used to analyze such data.

TABLE 4
Comparison of Ages

Method	*Estimate of age (in 10^9 years)*	*Remarks*
Extrapolation to $Pb^{207} = 0$	<5	Age of the elements
Extrapolation to $(U^{238}/U^{235}) = 1$	<6	Age of the earth's crust
Age of minerals (lead clock)	>2.6	" " " " "
Age of minerals (helium clock)	>2	" " " " "
Age of minerals (Rb-Sr chain)	>2.5	" " " " "
Pleochroic halos (alpha ionization effects in minerals)	>2	" " " " "
Terrestrial Pb isotopic ratios	3.4	" " " " "
Meteoritic Pb isotopic ratios	4.5	" " " " "
Cooling of the earth's crust	2–4	" " " " "
K^{40}-A^{40} decay chain	~4	Age of the atmosphere
Salinity of oceans	1–7	Age of ocean
Age of moon (tidal effects)	>2–4	Age of solar system
Age of sun	~5	Age of galaxy
Star clusters	4–5	Age of galaxy
Galaxy clusters	2–4	Age of universe
Recession of nebulae (expanding universe)	3.8	Age of universe

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SOME IMPROVISED APPARATUS

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MANY and varied are the reasons which may prompt a student to design and build a piece of scientific apparatus; many and varied are the choices he may make as to what he will build and how; and, indeed, many and varied are the reactions we teachers may experience upon sight of the finished products.

In this school, some of the reasons which prompt our students to improvise, duplicate, and invent apparatus include the following. The youngsters may wish to participate in a Science Fair, so they plan and build a piece of apparatus that will be useful in the laboratory after the competition. Perhaps the Science Research Club wants to do some work which requires specialized apparatus, and, lacking the funds required to purchase it, they attempt to duplicate it, patterning their product after a picture in a magazine or catalogue. Again, the student may be fascinated by some machine, process, or reaction, and thus may start his work from sheer interest. A fourth cause may be a desire to build a model that the teacher can use in a demonstration for the science classes.

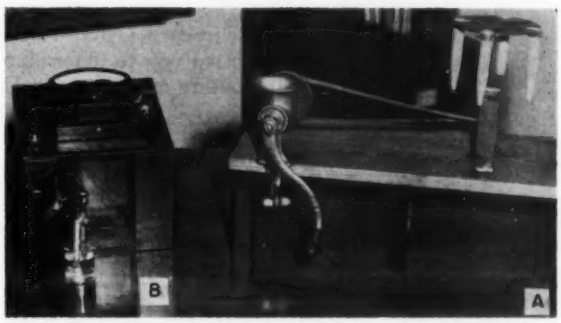
Some of the useful pieces of apparatus that the students in our high school have constructed are described below.

(1) *Hand Centrifuge.* This device, (*A*) in the illustration, was made from a discarded meat grinder which was attached to a small table built from scrap wood and pieces of iron found in a shop. The grinder was attached to a shaft which turns the head by means of a belt. The aluminum holders and glass centrifuge tubes were purchased from a supply house. This won a first award in the Philadelphia Science Fair.

(2) *pH Meter.* This instrument (*B*) is the latest addition to our laboratory. The case houses three tubes, an amplifier, and a cell, which are connected to the voltmeter (visible in the picture) which is in turn connected to the electrode assembly shown below. Plans for the model were made by the builder after considerable research on pH meters and some examination of schematic diagrams. This won a special award in the 1954 Philadelphia Science Fair.

(3) *Emulsifier.* This useful piece of equipment, which serves very suitably as a shaker as well as an emulsifier, was also built for an exhibit. It consists of a small table to which was attached a rectangular box containing four bottles (half-pint milk bottles) mounted on springs. This box is made to move up and down as the handle is turned, thus causing the bottles to vibrate and their contents to be emulsified or shaken, as the case may be.

(4) *Tin-can Planetarium.* This article is useful as



a demonstration piece in general science classes (if the room is dark enough). The builder got his idea from Watson's article in *The Science Teacher.*[1] As an exhibit this won a third award in the Philadelphia Science Fair.

(5) *Stirrer.* A broken-down stirrer used in a drug store for making milk shakes was secured, reconditioned, mounted on a base, and put to work in the laboratory.

(6) *Cooling Box.* The purpose of this device is to provide a cooling chamber for materials whose temperature we wish to keep below 0°C. The box (an old pneumatic trough, small size) contains a mixture of acetone and dry ice and has a fitted top containing holes large enough to admit test tubes containing the experimental material. This article has the disadvantage, however, of needing constant attention because the mixture lasts only for a limited time.

(7) *Print Box.* A member of the school Photography Club found it feasible to add this box to our collection. It is fashioned as is any ordinary print box on the market. Two electric sockets are in the box, one on the side wall and one (for the red lamp) on the floor. When the plug is attached the red light goes on. A switch is provided on the side for the other lamp.

(8) *Apparatus for Sending Sound on a Beam of Light.* This was erected primarily, of course, as an exhibit, but it is useful and interesting for demonstrations in science class as well. The materials used in this exhibit are: a radio, a flashlight, a photoelectric cell, and an amplifier. The entire setup is encased in a wooden frame which is covered with protective screening. It is arranged as follows: the flashlight is attached to the audio output of the radio, encased on the right side of the exhibit box, and made to shine directly on the photo cell, which is connected to an amplifier on the left side. Passing an opaque object through the beam of light causes variations in the sound.

[1] WATSON, F. G., *The Science Teacher,* 17, 180–83 (1950).

STUDIES OF EGYPTIAN BRONZES

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(Translated by Ralph E. Oesper)

Figure 1. Isis with Her Son Horus

AN INVESTIGATION whose objective was to determine the nature of the materials used to prepare early Egyptian *objets d'art* involved the qualitative analysis of a number of metal statues. The specimens used belong to the Kunsthistorisches Museum in Vienna; Dr. E. Komorzynsky, the director of the Egyptian-Oriental collection, furnished the cultural information regarding these pieces. The eight samples examined were derived from three statuettes of Osiris; a statuette of Isis; one of Isis with her son Horus (Figure 1); a statuette of Anukis (Figure 2); three statuettes representing, respectively, Harpocrates, an ibis, and the hawk-headed Ra; a fragment, namely an arm with a lotus flower on which is seated Harpocrates (Figure 3). The figures were votive offerings from the sixth century B.C.; the arm is younger and dates from the Greco-Roman period.

Since the great archeological value of the objects precluded their being subjected to any visible damage, only small amounts could be removed for the analysis. The necessary samples were taken by the method developed by Strebinger and Holzer.[1] A microscope slide with a roughened section in its center was rubbed across the specimen several times. Several micrograms of the metal thus produced a streak on the rough glass surface. This method of sampling proved its value in many cases; the effects on the specimens were scarcely noticeable.

The metal was dissolved from the slide by means of a drop of aqua regia. The solution was brought to dryness, and the residue was taken up in 2 *N* hydrochloric acid. It was found that if the concentration of nitric acid in the aqua regia were too high some of the tin might be left undissolved, a result that could be clearly detected by examining the rough glass surface with a magnifying glass. In every case, however, part of the tin was converted into the cationic form by the hydrochloric acid of the solvent and could be detected in the usual way in the course of the hydrogen-sulfide treatment.

Obviously, only microchemical methods could be employed in the successful analysis of the drop of solution available. The procedure used was the one recently described by the author.[2] The method was somewhat modified to fit this particular case, and consequently the essential features are described here. The technique, which the author has named the "ring oven" method, permits the analysis of a single drop (1–2 mm.)[3]. In this study the ions possibly present were: Pb, Bi, Cu, Cd, Sn, Fe, Zn, Ni, and Co.

The drop derived from the sample was placed in the middle of a 7-cm. filter paper (Schleicher & Schüll No. 589). All of the Bi, Cu, Pb, and Sn was fixed in

[1] STREBINGER, R., AND H. HOLZER, *Mikrochemie*, **8**, 264 (1930).

[2] WEISZ, H., *Mikrochim. Acta*, **1954**, 140; 376.

Figure 2. Anukis

position by treatment with hydrogen sulfide. This step was conducted in the all-glass apparatus shown in Figure 4. The flask contained zinc sulfide, and the dropping funnel was charged with sulfuric acid (1:1). The tubes *A* and *B* were provided with plane-ground ends and during the passage of the gas these flanges were pressed together by two spiral springs. The filter paper carrying the fleck to be analyzed was placed between the ground surfaces of the funnel-shaped tubes. The acid was then allowed to enter the flask and the resulting hydrogen sulfide drawn through the fleck by applying suction with the water aspirator, the suction being controlled with the stopcock *C*. Complete precipitation was secured in a very short time, with no annoyance from the odor of the gas.

The paper was next transferred to the second apparatus, the ring oven, shown in Figure 5. It consisted of a cylindrical heating block made of aluminum. A hole 22 mm. in diameter passed through the entire block, whose height was about 35 mm. and diameter about 55 mm. A heating element was built into the block. In operation, the temperature on the surface of the block was kept at about 105°C. by means of a rheostat. The narrow tube *B*, which served as a guide for a capillary pipet, pointed precisely at the center of the hole in the block. The paper, carrying the fleck, now contained any lead, tin, copper, and bismuth as the respective sulfides, and also the other possible ions which were not precipitated. It was now placed on the heating block in such a position that the fleck lay directly below the opening of the tube, which was supported vertically a little above the paper. The latter was kept in position by weighting it with a porcelain ring.

A capillary pipet was used to deliver the necessary reagents to the paper. It was filled simply by dipping it into 0.1 *N* hydrochloric acid, and it was then passed through the guide tube. The acid flowed onto the fleck and dissolved the soluble sulfides (Fe, Ni, Co, Zn), and then passed through the capillaries of the paper. The liquid evaporated at the edge of the hole in the block and deposited its burden of dissolved salts as a ring. The fleck was then washed five to ten times with successive single drops of 0.1 *N* hydrochloric acid. This treatment effectively removed all soluble materials from the fleck, which were then accumulated at the predetermined place on the paper.

This process was tried out on a drop of iron solution and after drying the paper was sprayed with a solution of potassium ferrocyanide. The result was a sharp ring of Prussian blue the thickness of a pencil line. The area of the circle was distinctly less than that of the spots usually observed in this type of procedure. The inside of the circle was completely void of iron ions and consequently remained colorless when the developer was applied.

In this analysis the center of the paper contained a fleck made up of the mixed insoluble sulfides; on the outside was a ring containing all of the iron,

Figure 3. Harpocrates Seated on Lotus Blossom

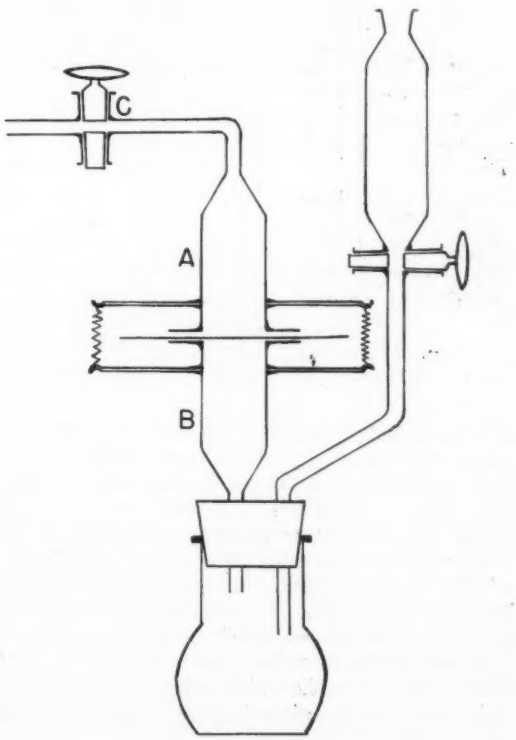

Figure 4. Appartus for Hydrogen-Sulfide Generation and Treatment

nickel, cobalt, and zinc, while the intervening "neutral zone" was entirely free of metal ions.

The paper was dried and removed from the block. The sulfide spot was cut out with a punch and the ring on the remaining paper designated as Ring I.

The small punched-out circle of filter paper containing the sulfides was fumed over bromine water to oxidize all the sulfides to sulfates. After the mixture had been made ammoniacal by an analogous treatment, the little disc was dried to insure the fixing of the tin. The disc was then placed in the center

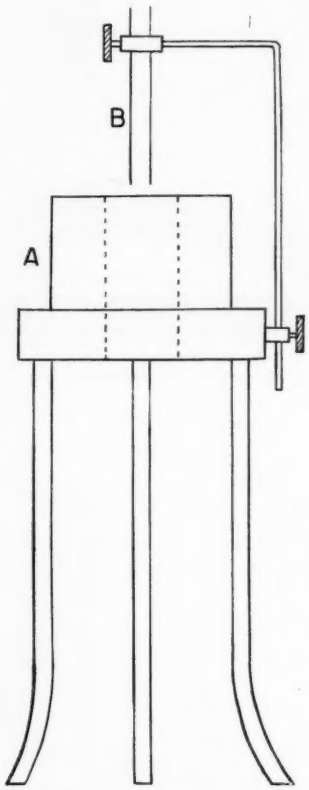

Figure 5. Weisz "Ring Oven" and Guide Tube

of a fresh filter paper and again leached on the ring oven, the extracting liquid now being ammonium hydroxide (1:5). All of the copper and cadmium was thus transferred to the outer zone of the underlying paper, the disc acting precisely as though it were a fleck. It now contained all the lead (as sulfate) and all the tin and bismuth (as hydroxide or basic salt). The new ring—Ring II—contained all of the copper and cadmium concentrated in a sharp ring zone. The punched-out section was then laid on a fresh filter paper and washed with yellow ammonium sulfide. This treatment transferred all of the tin into the outer ring zone of the supporting paper. After drying, this filter paper contained, in Ring III, all of the tin again as sulfide, while the punched-out section contained all of the lead and bismuth, also as sulfides.

In this way, all of the ions were separated into four groups of such nature that they could be detected in the presence of one another. The entire procedure of this separation required about 15 minutes.

The three rings were next cut into several sectors. When developed with the appropriate reagents, the individual ions, when present, yielded strips of the corresponding colors. All the tests were conducted on paper by means of identification reactions which, though not original, were modified for this particular purpose. It would go far beyond the bounds of this paper to describe the various identification reactions in complete detail; only the essentials will be given here. The cited publications should be consulted to learn the method of conducting the tests for the individual ions on the various sectors of filter paper. They also contain more explicit information regarding the actual analytical procedures employed in this type of analysis.

The following were detected in the sectors of Ring I: iron with potassium ferrocyanide, nickel with dimethylglyoxime, zinc with ammonium mercury thiocyanate and cobalt acetate, and cobalt with α-nitroso-β-naphthol.

The sectors of Ring II were tested for copper with rubeanic acid, and cadmium was sought with hydrogen-sulfide water followed by development with silver nitrate.

Zinc was found in the sectors of Ring III; the reagent was morin.

The small disc contained lead (sodium rhodizonate), and for bismuth (after destruction of the sodium rhodizonate) the usual test was made with sodium stannite and lead chloride.

The analytical findings are compiled in the table. The specimens without exception were bronzes. It is remarkable that no tin was found in three cases. It may be assumed that the quantities of tin in these three alloys were below the detection limits of the test employed. The lead content of the specimen of later date (No. 8) was distinctly higher than that of any of the others. However, no essential qualitative difference could be established in the composition of the pieces originating from the various places.

Statuette	*Pb*	*Bi*	*Cu*	*Cd*	*Sn*	*Fe*	*Zn*	*Ni*	*Co*
1. Osiris	+	+	+	−	+	+	+	−	−
2. Osiris	+	+	+	−	−	−	−	−	−
3. Osiris	+	+	+	−	+	+	+	−	−
4. Isis	−	−	+	−	+	+	−	−	−
5. Isis	+	+	+	−	−	+	+	−	−
6. Anukis	+	+	+	−	−	+	−	−	−
7. Triple	+	+	+	−	+	+	+	−	−
8. Fragment	++	+	+	−	+	+	+	−	−

QUANTIZED EDUCATION[1]

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FROM time to time there have appeared in THIS JOURNAL analyses of teaching techniques, studies on presentation of subject matter, and evaluations of various curricula. In this paper the general field of education is reviewed in the light of some well known principles of quantum mechanics.

The modern educational process can be thought of as consisting of a series of discrete steps. Hence the title "Quantized education." Instead of energy levels we shall refer to educational levels, and we shall consider the steps involved in reaching the upper quantum levels which represent the state of an educated person.

First, let us define our educational unit. The unit employed is the *credit*. A certain number of credits is required before a student reaches a next higher educational level (say, freshman→sophomore→junior→senior; or, in grade school, first grade→second grade →etc.).

Initially, the intent of the credit as a unit was to represent a "packet of knowledge." In this respect the credit is a perfectly proper unit when considering the quanta involved in changes in educational levels. Unfortunately, there has, in recent times, been a trend toward equating this unit with the unit of time spent in a classroom for which, it would seem, there does not exist a conversion factor. Spending four years in a high school or college is not the same as obtaining a high-school or a college education.

Two examples will serve to illustrate this point.

(*a*) At the end of the freshman chemistry course in a large midwest university, the students (about 350) were asked to evaluate the course and their instructors. The replies covered a complete spectrum in evaluating the course, ranging from, "Just a rehash of high-school chemistry" to, as one student descriptively put it, "It snowed me!" Each student had had a year of high-school chemistry which was a prerequisite for admission to this course. True, students have different abilities. But the point is that equal time of attendance does not signify equal accomplishment.

(*b*) An extensive study of several aspects of training has been completed recently by the commission on Human Resources and Advanced Training.[2] A comparison of college graduates at various schools, some of which admit their students selectively, shows a clear distinction in performance among the various groups. This result is to be expected. But again, it emphasizes that a unit based upon time may be misleading in considering educational levels.

In the matter of selection, the private schools may be at an advantage since they can set their own standards for entrance. However, this does not mean that their standards are alike. Neither does it mean that their standards do not fluctuate. They do, the variation undoubtedly being dependent upon the numbers applying for admission. On the other hand, many state schools are required by law to admit all high-school graduates from their state. Hence, to some extent, the standards are set by the high schools. The fact that a unit based upon time rather than accomplishment is used in many schools is a point of concern to most state universities.

The graduate schools to a large extent are more aware of the proper unit by which to measure educational levels. The graduate school confers its degree after a certain intellectual achievement has been demonstrated, regardless of the time required to attain this level. However, even here there may be areas of study in which the time factor receives undue emphasis.

Let us now consider other aspects of quantized education. And let us focus attention on the colleges which, at present, are faced with the problem of a large increase in enrollment in the next five years, with an estimated doubled enrollment by 1970. Unless facilities are expanded, the Pauli Exclusion Principle is sure to come into effect. Students will have to wait for a vacancy, and admittance, even at state universities, may be subject to strict Selection Rules.

The college student is bombarded in the classroom by quanta of education of 50-minute duration. When the bell rings irradiation ceases (even though the teacher is in the middle of a topic, and sometimes even in the middle of a sentence). After a year of such irradiation the student may then "jump" to the next educational level. Now some means is essential to determine whether or not the student has really been irradiated and has attained the higher level. The experimental criterion is to obtain "emission spectra" through examinations. Generally, emission is observed just at the close of the irradiation period, *i. e.*, at the end of the course. As a consequence, no true measure of the half-life of a class in this higher educational level is evaluated. It may be that, by cramming, students may show passable emission spectra, although the half-life in this excited state would last probably no more than a few days. The optimum half-life for the class, of course,

[1] Adapted from a presentation before the Northwestern University chapter of Phi Lambda Upsilon on the occasion of its annual Meeting in Miniature, May 15, 1954.

[2] WOLFLE, DAEL, "America's Resources of Specialized Talent," Harper and Brothers, New York, 1954, pp. 146–7.

would extend to senility. In most cases, the half-life lies somewhere between these extremes.

On the graduate level an appreciable half-life in the higher levels is required, since spectra are taken at various intervals to permit comprehensive scanning of the student's knowledge and ability.

We might say that the different eduational levels apply to major transitions, comparable to changes in electronic levels. Now the goal of education is to excite the students into the highest of these levels during the period of academic training. This requires taking courses of substantial content where irradiation by proper educational quanta is to be expected. But there is offered in current curricula a large number of courses which do not require the highest educational endeavor. Many students flock to these courses either because these courses are a "snap" or because department requirements force them to do so. This magnetic influence—the Zeeman effect—can, at best, bring out the fine structure of a particular educational level. Many years may thus be spent within the confines of this level and no amount of rotation or vibration will effect a major transition.

More and more people in all walks of life *want* to be quantized. That is, they wish to obtain a degree to signify a level of accomplishment. This desire for improvement is commendable in itself. But frequently the bulk of effort has been aimed at the minor rather than major transitions. A consequence has been an upsurge in survey courses and short courses.

The "snap" course which utilizes infrared radiation on a system which requires ultraviolet radiation cannot be successful. If this process is ineffective we may ask, "What about using photons of high energy?" Hurling at students sizeable quanta of knowledge, which may be completely out of their range of absorption, again is hardly likely to produce results. Thus, teaching the theory of relativity to a kindergarten class is quite unlikely to prove effective.

In an effective radiation process a high quantum yield should be obtained. This is dependent upon the following:

(*a*) If the system is fixed, the yield will depend upon the nature of the irradiation. That is, for students of a fixed ability, progress will depend upon the educational quanta to which they are exposed, *e. g.*, microwaves in kindergarten and X-rays in graduate school.

(*b*) If the radiation frequency is fixed, the yield will depend upon the system investigated. That is, for particular educational quanta, progress will vary with the type of student. This does occur, of course, as is evident by the distribution of grades in any program.

Much of the present controversy in education is based on the question of what constitutes the effectiveness of an educator. Should he have a knowledge of teaching methods or subject matter? This is comparable to asking whether matter is composed of waves or particles. Without regard at the moment to the extent of knowledge in each area, every teacher employs some teaching method and relies on certain subject matter. There is a duality here, the parts of which cannot be separated. Perhaps knowledge of teaching methods will appear most pronounced in considering the effectiveness of a kindergarten teacher, but knowledge of subject matter is certainly most critical in teaching a graduate course effectively.

No educator can have complete command both of teaching methods and subject matter. In short, no teacher is perfect. At best an educator may approach this state, but some uncertainty in his ability will always remain. We might state the uncertainty in the following way:

$$\Delta \text{ teaching methods} \times \Delta \text{ subject matter} \simeq h$$

where Δ represents uncertainty and h is a constant which is a measure of the most effective teaching possible (units of action). Excessive time spent on developing teaching methods would be at the expense of acquiring subject matter, and the converse would also be true. Assuming that the study of teaching methods is not repetitious, this might create the impression that it makes little difference as to direction of effort. However, that is not the case. The constant h represents the limiting effort in teaching, and the efforts of most teachers would be far from this limit. For kindergarten teaching the uncertainty in subject matter required is relatively small, and perhaps to focus attension upon teaching methods would be profitable.[3] For the graduate course, however, the need for reducing uncertainty in knowledge of subject matter is so great that it takes primary consideration. It may take several hours to organize and plan an effective lecture, but it takes several years to gain an understanding of the material.

One final aspect pertinent to college training may be mentioned: namely, the college curriculum. Let us consider students moving freely on a college campus and compare this to the motion of electrons in a metal. The students occupy educational levels (from freshmen to seniors) and progress from lower to higher levels by acquiring sufficient educational quanta. What of those students who are not able to make the "jump" over the forbidden zones? In the case of metals, the introduction of impurities creates new energy levels which enable an electron in a lower energy level to enter a region previously forbidden, and the electron may get to higher levels through a series of "jumps" each of which does not require excessive quanta of energy. In many colleges "impurities" have also been added in the form of "diluted" courses. Now the less capable student can make progress also, although at the end of four years he will not have attained the level of his more able classmates.

Is there a justification for this? There is to some

[3] This discussion is limited solely to teaching effectiveness within a given educational level, and no effort is made to consider the effect of excessive time spent in acquiring teaching techniques on the teacher as a well-rounded, educated individual. That is, the vocational rather than the educational aspect is considered. In this sense the Uncertainty Principle is restricted for consideration at each educational level.

extent. The introduction of impurities in a metal, *when properly controlled*, can give results of a very useful nature. Similarly, a carefully controlled curriculum may serve a purpose in tapping the potential supply of trained personnel in widely differing areas of interest. But expert control must be exercised since wanton adulteration would doom to failure the desired result.

We can hope that educational irradiation will remain in the hands of experts.

A JIG FOR MAKING ATOMIC MODELS

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THE visualization of the spatial arrangement of atoms in a molecule or crystal becomes difficult for many structures of high coordination, particularly when several different interatomic distances are involved and the angles are no longer simple. It is often advisable to make a three-dimensional model to scale in order to see the atomic arrangement in proper perspective. The authors have devised a simple hand-operated instrument for boring holes in cork balls at positions of interatomic bonds. The balls are then put together with wires of appropriate length to form the desired structure.

Similar machine-operated instruments using wooden balls have been described by Buerger[1,2] and Butler, and by Terpstra.[3] While the same basic principle is used, the instrument described here is simpler, less expensive to construct, and easier to operate. It would serve more readily as a desk instrument for constructing models out of small cork balls.

DESCRIPTION OF THE APPARATUS

The instrument devised, shown in Figure 1, is simply a two-circle goniometer, with a cork ball mounted so that its center lies on the horizontal and vertical axes of rotation. The ball remains stationary while a small hand-drill mounted on the vertical semicircular scale is rotated about the vertical axis (through any angle up to a full circle) and the horizontal axis (through any angle up to a half-circle) to the position desired. A few turns of the drill, and the cork ball "atom" has a hole ready to receive one of its wire "interatomic bonds." Holes are bored at all bond positions on the upper hemispherical surface of the ball; the ball is then inverted and holes bored at the remaining bond positions. A cork ball is prepared in this way for each atom. The structure is then completed by putting together the cork ball "atoms" with pieces of wire cut to the proper lengths for the interatomic distances, remembering that a bond length is measured from center

Figure 1

[1] BUERGER, M. J., *Rev. Sci. Instr.*, 6, 412–16 (1935).
[2] BUERGER, M. J., AND R. D. BUTLER, *Am. Mineralogist*, 21, 150–72 (1936).
[3] TERPSTRA, P., *Natuurw. Tijdschr. (Belg.)*, 21, 283 (1939).

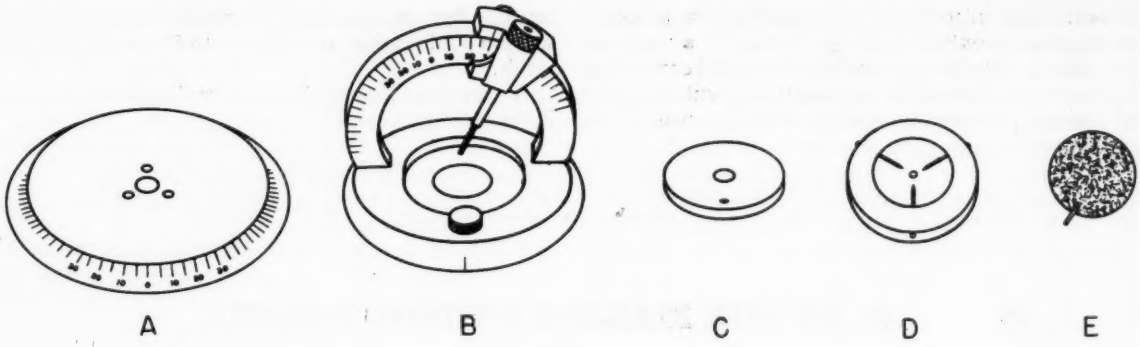

Figure 2

to center of the atoms, so that radii of the cork balls must be considered in cutting the wire "bonds."

The instrument in more detail is shown in the sketches of Figure 2. The base is a brass cylinder 3.5 in. in diameter and 3 in. high; it is hollowed out to a wall and top thickness of $^1/_2$ in. The height and massiveness are needed for easier manipulation and stability of the instrument. Fastened to the base by screws is the angular scale (Figure 2*A*) for rotation about the vertical axis. Figure 2*B* shows the angular scale for rotation about the horizontal axis. This scale is fastened to a circular plate which fits over the plate of Figure 2*A* but is not fastened to it. It is held in position by the base (Figure 2*C*) for the ball holder. This base is fastened by screws to the scale plate of Figure 2*A*, but is not fastened to the circular plate of Figure 2*B*, which leaves this plate free to rotate with respect to the sample base and the instrument base. The ball holder (Figure 2*D*) fits into the base 2*C* and is held stationary by a pin. The cork ball (Figure 2*E*) fits into the holder and is held in position by a vertical pin and three horizontal pins. Several ball holders may be made to accommodate different sized balls. The drill is shown in Figure 2*B*, attached so that it may be moved along the scale. With this arrangement the drill can be rotated about the vertical axis by motion of the entire assembly shown in Figure 2*B*. Rotation about the horizontal axis is achieved by motion of the drill along the scale to which it is attached. During these motions the ball remains stationary with respect to the base of the instrument. Thumb screws are provided for locking both the horizontal and vertical angles.

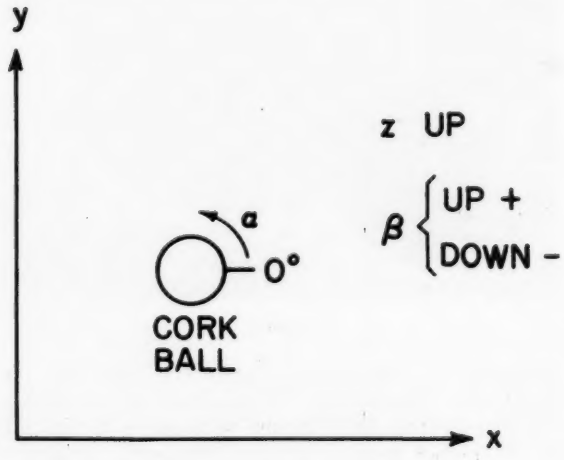

Figure 3

CALCULATION OF ANGLES

Two angles are needed in order to locate each bond position on the cork balls: an angle α, the rotation about the vertical axis, and β, the rotation about the horizontal axis, each measured from a chosen zero on the cork balls. These can be determined as follows. Let us assume that the positions of all atoms are known with respect to a rectangular coordinate system, where the unit of distance is the same along the three axes, usually one Å. This information will be known or easily calculated for the atomic arrangement studied. Now let the cork ball zero be related to this coordinate system as shown in Figure 3. If $x_0y_0z_0$ refer to the atom under consideration, and a bond to atom xyz is being located, then the angles will be given by the following equations:

$$\tan \alpha = \frac{y - y_0}{x - x_0}$$

$$\tan \beta = \frac{z - z_0}{\sqrt{(x - x_0)^2 + (y - y_0)^2}}$$

and the bond length l will be:

$$l = \sqrt{(x - x_0)^2 + (y - y_0)^2 + (z - z_0)^2}$$

It is well to calculate and list systematically all angles and bond lengths needed for the arrangement before starting the construction.

Figure 4 shows models made with this instrument of the four different coordination figures in the alpha-manganese structure.

ACKNOWLEDGMENT

The authors wish to thank Dr. J. S. Kasper for critical reading of this paper.

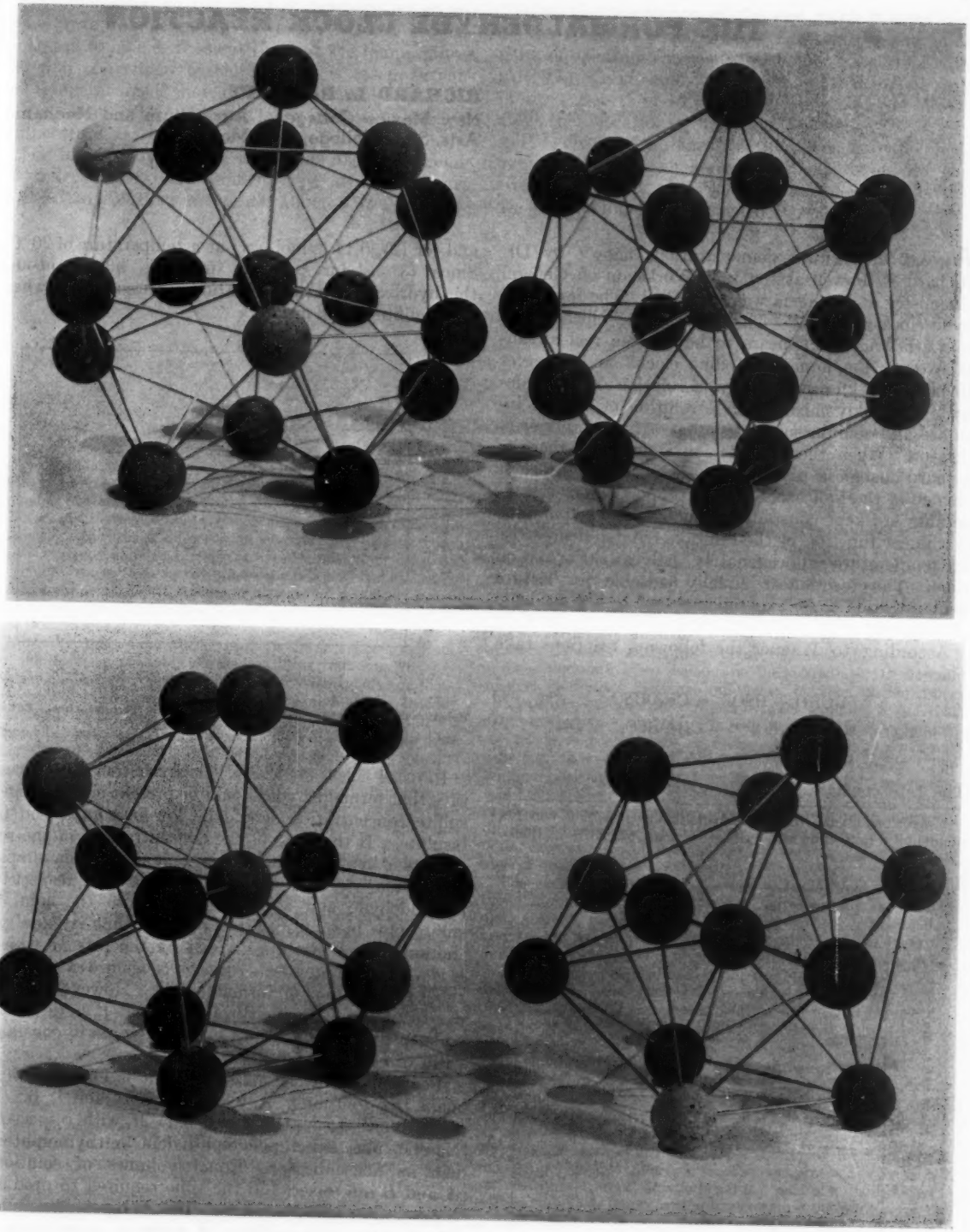

Figure 4

THE FORMALDEHYDE CLOCK REACTION

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Among the lecture demonstrations shown by Dr. Richard E. Powell at the 1953 Workshop on General Chemistry at Pasadena was one called "The formaldehyde clock reaction." This experiment, which is due to Carl Wagner,[1] appears to have some real advantages over the familiar "Iodine clock" and deserves to be better known. Briefly, a solution of formaldehyde is quickly mixed with a solution of sodium bisulfite and sodium sulfite together with a suitable indicator. When the bisulfite ion is used up there is a sharp change in pH which is signalized by the color change of the indicator. If the proportions of the reactants are kept constant the indicated reaction time is a linear function of the dilution. A ten-degree rise in temperature approximately halves the reaction time. The reaction is equally suitable for lecture demonstration or for experiments done by the students themselves.

According to Wagner the following reactions take place:

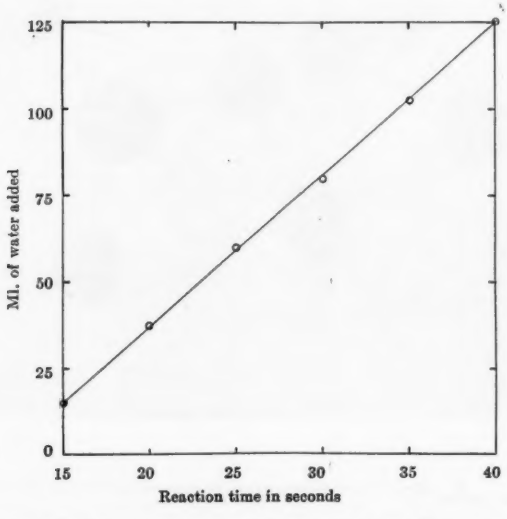
$$HCHO + HSO_3^- = CH_2OHSO_3^- \quad (1)$$

$$H_2O + HCHO + SO_3^{--} = CH_2OHSO_3^- + OH^- \quad (2)$$

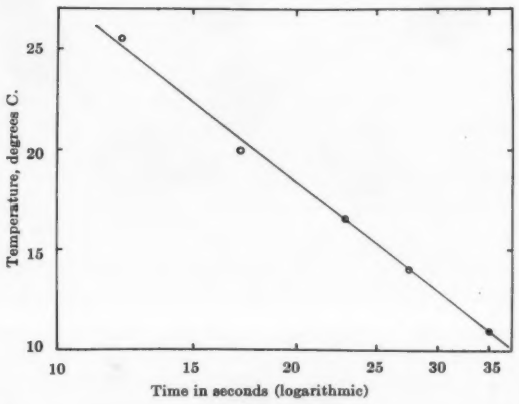
$$OH^- + HSO_3^- = SO_3^{--} + H_2O \quad (3)$$

The rate constant for (1) is given as 2.8 l./mol. sec. and for (2), 0.14 l./mol. sec. at a temperature of 20°C. Since (3) is for practical purposes instantaneous, the hydroxide ion concentration increases only when the bisulfite is used up.

[1] Wagner, Carl, "Über die Kinetik der Reaction von Formaldehyd mit Bisulfit und Sulfit," *Berichte*, **62**, 2873–7 (1929).



Relationship Between Reaction Time and Dilution for Mixtures Containing 50 ml. of Solution *A*, 50 ml. of Solution *B*, Plus Varying Amounts of Water. Temperature 20°C.



Relationship Between Reaction Time and Temperature. Equal Volumes of Solutions *A* and *B*

In using this system as a "clock reaction" it is necessary that formaldehyde should be present in excess, and sulfite concentration should be low in comparison to bisulfite. If the ratio of the concentrations of the reactants is kept constant the system simulates a simple bimolecular reaction which is first order with respect to formaldehyde and also with respect to the sum of sulfite plus bisulfite.[2] Since reaction time is equal to the amount of bisulfite divided by the rate at which it is used, dilution affects reaction time only as it affects the concentration of formaldehyde. However, in order to preserve simplicity of treatment it is desirable to keep the concentrations of all reactants in constant ratio.

For demonstrating mass action it is convenient to make two solutions: *A*, 0.3 *M* HCHO; and *B*, 0.2 *M* with respect to $NaHSO_3$ and 0.05 *M* with respect to Na_2SO_3, plus either phenolphthalein or thymolphthalein as an indicator. Equal volumes of solutions *A* and *B* are mixed and the time required to produce the indicator color is taken. This is repeated a number of times with addition of water in increments of perhaps a fourth or fifth of the original volume, and time is plotted against total volume.

[2] See "Rate, order, and molecularity in chemical kinetics," Laidler Keith, J., and Samuel Glasstone, J. Chem. Educ., 25, 382–7, (1948).

For demonstrating the effect of temperature on reaction rate the solutions are either diluted or concentrated to give convenient times at the temperatures you find convenient to employ. It is easier to control temperatures if they are kept reasonably near that of the room. The students then plot time against temperature.

The formaldehyde clock also lends itself to "chemical magic" and entertainment-type demonstrations. If the two solutions are made about 0.02 *M* in $Cd(NO_3)_2$, the completion of the end point is signalized by the formation of a white precipitate. Using three pairs of solutions, one with phenolphthalein, one with $Cd(NO_3)_2$, and one with thymolphthalein, a very pretty "Fourth-of-July" effect is produced. Probably other variations will occur to the reader.

The chief advantages of the formaldehyde clock over the well known iodine clock experiment are the greater simplicity of its kinetics, and flexibility in the use of indicators for showing the end point.

✦ ✦ ✦

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

INDUSTRIAL laboratories are already applying one of the more subtle techniques of modern nuclear physics. Nuclear magnetic resonance spectroscopy, discovered only eight years ago, is used to detect and distinguish between the nuclear particles present in a sample. In this it differs from conventional spectroscopy, which analyzes light and other radiation emitted or absorbed by the electron system surrounding the nucleus. In both cases, the problem is to identify the constituents of a sample, but of the two analytical techniques, n-m-r spectroscopy can draw the finer distinctions.

Normally, the atomic nucleus is almost impervious to any outside influence, because it is shielded by its surrounding electrons. Some nuclei, however, actually resemble small magnets and therefore can be acted upon by an external magnetic field. In addition, most nuclear species spin like a top. But, if a spinning magnet is placed in a strong magnetic field, it tends to flip over, and resists this tendency in exactly the same way that a spinning top resists the effect of gravity—by precessing. This is what happens when a top slows down; it tilts and in addition to spinning about its axis, it rotates slowly around the vertical. The stronger the disturbing force in either case, the more rapid this precession.

The precession rate of magnetized, spinning nucleus depends on the strength of the nuclear magnet, on the amount of its spin, and also on the strength of the external magnetic field. For example, if a sample of hydrogen is placed in a magnetic field of 10,000 gauss—readily attainable in the laboratory—the nuclei (protons) will precess 42 million times per second. This rapid precession, moreover, takes place in every hydrogen atom in a drop of water exposed to the magnetic field. Normally there is no way to detect it, but in 1946, Bloch at Standford and Purcell at Harvard, working independently, found that by applying a second magnetic field, alternating at precisely the frequency of precession, the effect could be observed.

One way to explain it is to say that the stationary magnetic field gets the spinning tops all lined up and precessing at the same rate. Then the alternating field causes them all to wobble in rhythm, or resonance as the physicist would have it. But it takes energy to do this, and Bloch and Purcell noted this absorption of energy from the alternating field whenever it was exactly in resonance with the precession.

For any given strength of the stationary magnetic field, each type of nucleus has its own characteristic precession frequency. Thus, it should be possible to identify the elements in a sample by first applying a steady field, then scanning over the suitable frequency range with the alternating field, and noting when energy is absorbed.

EQUIPMENT AVAILABLE

Instuments are now on the market for rapid, non-destructive n-m-r analysis of small liquid samples, including melted solids, solids in solution, and liquefied gases. The sample in a test tube is surrounded by a coil of wire connected to a source of radio-frequency current, and both are placed between the pole pieces of a strong magnet. When nuclear resonance occurs, energy is absorbed, and an external electric circuit detects this absorption—as a trace on a cathode-ray tube, for example. These instruments are used to identify components of a complex mixture and to determine the structure of a molecule.

Since the n-m-r effect depends on the strength of the nuclear magnet, and since there are differences between nuclei, n-m-r spectroscopy can also differentiate between isotopes, or different forms of the same element. Protons—hydrogen nuclei—happen to produce one of the strongest effects observed; n-m-r was first discovered with protons in water or paraffin. The fluorine nucleus is also easy to detect by nuclear resonance; n-m-r spectroscopy is often a sensitive way of detecting protons or fluorine nuclei in chemical compounds. Some nuclei, however, do not act like magnets and cannot be detected by n-m-r; such is the case with the most abundant isotope of oxygen, but most nuclear species can be analyzed.

The sample to be tested may be gaseous, liquid, or solid, though liquids are preferred. In both gases and liquids, random motion of the particles tends to average out any influence that may be exerted on a nucleus by its neighbors, but in gases the nuclei are relatively so few in number that the total effect is weak. In solids, where the positions of the neighbors are rigidly fixed, the influence of these neighbors shows up. As it depends in a predictable way on the arrangement of the neighbors, one can learn something about the local crystal structure by studying such disturbances of the normal effect; n-m-r spectroscopy of solids may thus be a help in crystal analysis. Hydrogen atoms, for example, are difficult to locate by other means, such as x-ray diffraction.

When the sensitivity of the n-m-r spectrograph is pushed as far as possible, one can observe minute differences caused by the chemical environment of the atom. Thus, for instance, it makes a perceptible difference whether the proton is surrounded only by other protons, or whether it is a part of a distinct chemical group. It is then possible to determine the position of the protons within a complex molecule and arrive at a better understanding of its structure. This particular aspect of nuclear magnetic resonance spectroscopy may provide an entirely new research tool for structural and organic chemistry.—*Reprinted from the Industrial Bulletin of Arthur D. Little, Inc.*

HUMANISTIC VALUES IN THE STUDY OF CHEMISTRY[1]

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Pick up almost any liberal-arts college catalogue and read the page entitled "Aims and Objectives." The chances are about ten to one that you will find some variation on the theme: "College students must learn how to live as well as how to make a living." The salaries offered to our graduates trained in chemistry leave little doubt that the study of our science is effective preparation for making a living but it is more difficult to demonstrate that the study of chemistry helps a man learn how to live. Many of us who teach in liberal-arts colleges are engaged in defending our discipline's place in a liberal education. Questions are raised concerning the value of chemistry to students not majoring in science. Less frequently, fear is expressed that chemistry majors do not acquire a set of values which stimulate them to participate actively in community affairs. I think we can answer these criticisms—and, indeed, profit from them—by giving some consideration to the humanistic values which lie in the study of chemistry.

To define humanistic values, the humanities, or humanism is very difficult. For the purposes of this paper, Walter Lippmann's statement, "Humanism signifies the intention of men to concern themselves with the discovery of the good life on this planet by the use of human faculties," is helpful. Humanistic values, then, are those which we must treasure if we are to discover and to live the good life.

The greatest obstacle to "the good life on this planet" is war. As stated in the Preamble to the Constitution of UNESCO, "Wars begin in the minds of men." We college teachers have, therefore, an important part to play in conditioning the minds of men to seek other ways of attacking human problems. If men are to avoid trying to settle their differences on the battlefield they must try to settle them at the conference table. Such efforts will involve all of us in continual controversy with men and nations whose views differ from our own. We are likely to live out our days in an atmosphere of tension and contention.

If the controversies which seem inevitable in the years ahead are to be fruitful they must be illumined by two ideals:

(1) The solution to any human problem can be hammered out in constructive controversy; the process may be slow and frustrating, but settlement by force is not only unnecessary but impossible in the long run.

(2) The solution—or amelioration—of a given problem can be achieved only by action based on understanding.

The first ideal arises chiefly from two attitudes toward man's intellectual activities:

(*a*) It is better to build a basis of agreement from differing points of view than it is to force the acceptance of one point.

(*b*) Man possesses the intellectual potential for continually improving his lot; we have by no means reached the limit of perfectibility; there are no insoluble problems—only problems of great difficulty.

The second ideal grows out of the following attitudes:

(*a*) In the "free market of ideas," truth will prevail.

(*b*) In constructive controversy, the purpose of the participants must be to discover truth rather than to win arguments.

(*c*) Truth is not achieved by making one's opponent appear ridiculous or by discrediting him on the basis of his race, color, creed, or political affiliation; only arguments—not people—can be discredited in constructive controversy.

(*d*) The proper function of words is to communicate ideas which will clarify issues, not confuse them.

(*e*) The nearer we approach a true understanding of a situation, the more effective will be our solution of problems rooted in it.

I believe that these attitudes have humanistic value. I believe that they can be cultivated in our students if we consciously bear them in mind as we teach our classes in chemistry. For example, the development of our present concepts of valency and chemical bonding illustrate that many differing points of view have served to advance our understanding of these complex phenomena. Had any one man's ideas been forced upon all chemists, what a stultifying effect this would have had! That truth is more important than winning arguments is dramatically illustrated in the continuing disclosure of the atom's mysteries by men who are ready to modify their arguments whenever new facts demand new interpretations.

That truth is not achieved by personal attacks on one's opponents is demonstrated by the spectacle of Russians repudiating the theory of resonance in chemical bonds because proponents of the concept

[1] Presented at the Symposium on The Cultural Values of Chemistry at the 126th Meeting of the American Chemical Society, New York, September, 1954.

are members of "a capitalistic, decadent, bourgeois society." That human intelligence is bounded by no lines of creed or nationality is illustrated in the growth of great unifying concepts like atomic theory and the periodic law. Two Englishmen and two Germans, two Italians and a Russian, a Belgian and an American shared in the basic work of establishing correlations between atomic weight and chemical properties. A perusal of the historical introduction in Smyth's report, "Atomic Energy," reveals that half a dozen Americans and an equal number of Englishmen and of Germans (together with three Frenchmen, one Dane and one Italian) were responsible for the basic discoveries upon which nuclear technology rests. Included among these scientists are Jews, Protestants, and Catholics, liberals and conservatives, socialists and communists.

The communicative power of well-defined words is amply demonstrated in chemistry. The study of our science offers a student the stimulating and exacting experience of expressing consistently constructed concepts in clearly defined terms. The kinetic-molecular theories of matter and electrochemical processes are examples which come to mind in this connection. In contrast, we may well consider the horrifying consequences of deliberately distorting the meaning of words to confuse controversial issues. George Orwell presents these consequences with nightmarish reality in his novel, "1984," in which "War is Peace" and the "Ministry of Love" is the agency which tortures minds and bodies until men believe that two and two make five.

Our increasing effectiveness in dealing with complex situations as our understanding of them approaches more nearly to the truth is illustrated by the fruitfulness of our present knowledge of gases and of solutions. Calling attention to the successive refinements of concepts and mathematical equations dealing with quantitative measurements in gaseous and liquid systems points up the value of continually striving for more precise truth.

I have used the word "truth" many times in the preceding paragraphs. A discussion of the nature of truth is beyond the scope of this paper. For our purpose, the following definition will suffice: Truth is the conformity of the mind's judgments with the actual states, conditions, and relations of external things. The study of chemistry offers many insights into the effective search for such truth but only five will be considered here.

(1) Establishing categories of things and ideas as we search for truth is useful for organizing our thoughts, but we must always bear in mind the arbitrariness of these categories.

(2) An approach to truth is verified by reference to demonstrable and communicable facts; it is *not* verified by the prestige or forcefulness of its advocate.

(3) Progress toward truth is piecemeal and men of widely varying abilities can contribute to it.

(4) Uncertainty need not lead to insecurity; relative truth is valuable and useful.

(5) Truth is approached by thinking, not by emotional reactions.

The usefulness—and the limitations—of establishing categories of things and of phenomena are readily illustrated by such classifications as those of elements into metals and nonmetals, compounds into acids and bases, and chemical bonds into ionic and covalent. The properties of metalloids, our continually broadening concepts of acid-base relations, and types of bonding intermediate between the transfer and the sharing of electrons serve as examples of the arbitrariness of our categorizing. They also emphasize the care we must exercise lest our organization of ideas cramp rather than liberate our thinking. The fact that, in the vast majority of cases, related natural phenomena tend to merge into a continuum as our knowledge of them expands should be borne in mind by every citizen as he struggles with social problems. In dealing with such problems, we are all too prone to believe that black is black and white is white and gray is an unthinkable condition.

That the truth of what a chemist says is verified by the facts he brings in support of his statements is illustrated by every development in chemistry since the days of Lavoisier. This attitude is so much a subconscious part of our approach to chemistry that we too often take it for granted, especially in teaching our introductory courses. We should emphasize this aspect of the development of truth again and again as our students build their understanding of both descriptive and theoretical chemistry. The growth of our knowledge concerning the nature of electrolytes and ionization is but one example of the development of a highly complex concept by the progressive modification of theory in order to interpret new facts. In chemistry there is no holy writ to serve as authoritarian dogma for the new generation. The ideas proposed by the intellectual giants of yesterday are barely recognizable as they are blended into the concepts of today's and tomorrow's chemistry. The long hiatus between Willard Gibbs' discovery of fundamental thermodynamic relationships of great potential value and the use of his discoveries by other chemists emphasizes that ideas must be communicated as well as verified if they are to contribute to the onward march of man's mind.

A quotation from Albert Schweitzer's autobiography, "Out of My Life and Thought," serves to underscore the attitude that winning arguments and promoting opinions in controversy may impede the discovery of truth.

> But the study of the natural sciences brought me even more than the increase of knowledge I had longed for. It was to me a spiritual experience. I had all along felt it to be psychically a danger that in the so-called humanities with which I had been concerned hitherto, there is no truth which affirms itself as self-evident, but that a mere opinion can, by the way in which it

deals with the subject matter, obtain recognition as true. The search for truth in the domains of history and philosophy is carried on in repeated endless duels between the sense of reality of the one and the inventive imaginative power of the other. The argument from facts is never able to obtain a definitive victory over the skillfully produced opinion. How often what is reckoned as progress consists in a skillfully argued opinion putting real insight out of action for a long time!

One of the severest social maladies of our time is pessimism. The material and spiritual devastation wrought by two world wars in thirty years and the continued conflicts in Korea and Indo-China have driven many men into despair for the future of their kind. If man ever needed faith in his ability to solve his problems, he needs it now. Too many men are saying, "There is nothing I can do." This wave of social pessimism must be counteracted by a surge of scientific optimism. We should point out how chemistry has contributed to solutions of social problems in the past, and show how chemists are now helping man in his struggle to make the most out of his earthly heritage. It is even more important to emphasize that anyone of moderate intellectual endowment can make his efforts count. Progress in our science does not depend on genius. In the words of Bertrand Russell, "The edifice of science needs masons, bricklayers, and common laborers as well as foremen, master builders, and architects." Chemists are optimistic about the future heights which they will conquer. We must infect workers in other fields with like optimism.

As chemical research discloses new vistas in the panorama of our science, we are fully aware that all things are not necessarily just as we envision them faintly and for the first time. A chemist does not believe in the absolute and unalterable truth of any of his working hypotheses but he works them none the less. Relative truth may not seem so satisfying as absolute truth but we need not feel insecure because we have not attained the absolute. So in attacking social problems which seem, in their immensity, to dwarf their counterparts in science, men need not waver because final answers are not immediately forthcoming. To quote Bertrand Russell again: "One of the greatest benefits that science confers upon those who understand its spirit is that it enables them to live without the delusive support of subjective certainty."

In these days of cold wars and hot arguments it is essential that we pursue the truth with calm, clear thinking. The heat of emotion may spur men to victory in battle, but winning the truth through tedious struggles at the conference table requires more light than heat. Nazi "thinking with the blood" swept Germany to the verge of conquering all Europe, but the cold, hard facts of manpower and production finally defeated her. The ranting of present day anti-intellectuals with their slurring innuendos about "the egg-head" and "the professor" must be answered by the loud, clear voice of reason. The battle of the battery additives and the ultimate vindication of Astin and his co-workers at the Bureau of Standards show that when scientists and other intellectuals speak with one voice they can be heard above the clamor of the crowd. In teaching chemistry we should emphasize again and again that wishful thinking and pleasant myths impede the discovery of truth. We must inculcate in our students a passionate objectivity in facing facts.

The study of chemistry abounds with humanistic values. Without fundamental changes in his courses, any chemistry teacher can help his students acquire the attitudes: that the solutions of man's problems can be worked out on the basis of truth achieved through constructive controversy; that arguments in such controversy must stand or fall on the strength of the evidence—not the qualities of the men—supporting them; that evidence must be evaluated thoughtfully and not emotionally; that relative truth is useful and can be achieved by the cooperation of all.

DU PONT FELLOWSHIPS FOR TEACHERS OF CHEMISTRY

SAINT LOUIS UNIVERSITY has been awarded an $8100 grant from E. I. du Pont de Nemours and Company for the general support of its Institute for the Teaching of Chemistry.

A grant of $4500 will provide 12 fellowships for high-school and junior-college chemistry teachers, enabling them to attend the university's Institute for the Teaching of Chemistry during the summer of 1955. The fellowships provide tuition of $100 and a living allowance of $180 for the student.

In addition, a grant of $3600 will provide two fellowships for the support of qualified, recent college graduates who wish to work toward an M.S. degree in the teaching of chemistry during the academic year 1955–6. The year's study will prepare recipients of the fellowships to teach chemistry, physics, or mathematics in a secondary school. Each fellowship will provide $450 tuition and a stipend of $1200.

The Institute for the Teaching of Chemistry was founded in 1950 to meet the rising need for correlation between the fields of education and science. Up until the formation of the Institute there was no program designed to fill the needs of the secondary-school teachers, since the traditional research master's degree in chemistry is directed toward the preparation of the professional chemist rather than the teacher. The Institute is administered by the chemistry department with the cooperation of the related science departments and the department of education.

There are three phases in the Institute's program. It offers a B.S. degree in the teaching of chemistry, an M.S. degree in the same field, and a six-week summer program for M.S.-degree candidates and for in-service training of teachers.

Qualified applicants may write to: Dr. T. A. Ashford, Director of the Institute for the Teaching of Chemistry, Saint Louis University, for further information concerning the fellowships and the Institute.

INTRODUCING STEREOISOMERISM

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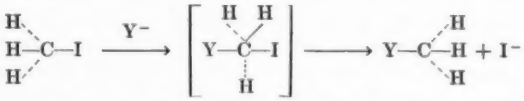
THE subject of stereochemistry is treated in standard undergraduate organic chemistry books in a single chapter usually located in the central portion of such texts.[1] Outside that chapter, reference to stereoisomerism is generally limited to the discussion of carbohydrates and a brief word under Amino Acids.

A twofold criticism can be made against this time-honored presentation of stereochemistry. First of all, in this arrangement the student is not introduced to this aspect of organic chemistry until the closing lectures of the first semester, and, secondly, the topic is presented in a manner isolated from the remainder of organic chemistry. This means that in a course which presents aliphatic chemistry in the first semester and aromatic chemistry in the second, stereoisomerism is discussed at the tail-end of the study of aliphatic chemistry and usually not considered further in the second semester. This leaves the impression with the student that this type of isomerism is an odd fact to be mentioned, but with which one does not have to be concerned in organic chemistry in general.

In recent years an increasing amount of theoretical organic chemistry (organic reaction mechanisms, etc.) has been introduced into elementary organic chemistry courses.[2] This shift makes it increasingly desirable to abandon the above-mentioned practice with respect to teaching stereochemistry.

In the undergraduate organic chemistry course given at Duquesne University the subject of stereochemistry is introduced in the following manner. In the discussion of the reactions of alkyl halides, one of the first classes of compounds studied, the displacement of the halogen atom by nucleophilic reagents is mentioned and illustrated by various examples such as hydroxide, acetate, and iodide ions. Also introduced at this point is the concept of reaction mechanism, which in this particular example consists of attack by the nucleophilic reagent on the carbon at which reaction is occurring from the back side of the bond which is being broken, with inversion of the three groups attached to the center of reaction.[3] This is illustrated with methyl iodide:



It can be pointed out that if $I^- = Y^-$ then the product and the starting material are identical and can be superimposed upon each other.

The next step is to go through the same reaction with a halide such as sec-butyl halide (bromide or chloride) instead of the methyl iodide used previously:

Now stating that $Y^- = Br^-$, we find that the product has the same empirical formula and the same groups attached to a particular carbon as the starting material, but that the two structures cannot be superimposed upon each other.

Thus, by this approach we have come directly from the reaction of the alkyl halide by way of consideration of the mechanism by which reaction occurs, to an example of stereoisomerism. Therefore, this is a smooth transition for introducing the student to the basic concepts of stereoisomerism. From there on stereochemistry is handled in the discussion of all other functional groups and more details are given to the student as the need arises.

This early introduction of stereochemistry makes it possible to present stereochemical evidence of reaction mechanisms to indicate the racemising effect of groups such as an alpha-carbonyl group and other effects related to stereochemistry. Furthermore, the study plan outlined above gives the student a deep appreciation for this aspect of organic chemistry, which is becoming as important in theoretical work[4] as it has been in the chemistry of natural products for many years.

[1] Examples: FIESER, L. F., AND M. FIESER, "Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, **1950**, Chap. 11, pp. 246–91; RICHTER, G. M., "Textbook of Organic Chemistry," 3rd ed., John Wiley & Sons, Inc., New York, **1952**, Chap. XVII, pp. 331–50; DESHA, L. J., "Organic Chemistry," 2nd ed., McGraw-Hill Book Co., Inc., New York, **1952**, Chap. 17, pp. 322–40; CONANT, J. B., AND A. H. BLATT, "The Chemistry of Organic Compounds," 4th ed., The Macmillan Co., **1952**, Chap. 13, pp. 245–58.

[2] NOLLER, C. R., "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, **1951**; BREWSTER, R., "Organic Chemistry," 2nd ed., Prentice-Hall, Inc., New York, **1953**.

[3] ALEXANDER, E. R., "Principles of Ionic Reactions," John Wiley & Sons, Inc., New York, **1950**, p. 81.

[4] REMICK, A. E., "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley & Sons, Inc., New York, **1949**, Chap. IX, pp. 288–341.

THE RADIOACTIVITY OF THE HUMAN BODY

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Among the elements that are essential constituents of the human body, the one naturally occurring, long-lived radioactive nuclide is, of course, K^{40}. There are two short-lived radioactive nuclides among these elements, however, which are also naturally occurring since they are continually produced by natural transmutative processes initiated in the atmosphere by cosmic rays. These are C^{14} and H^3. All three are beta-emitters, C^{14} and H^3 entirely so, K^{40} to the extent of 90 per cent, its remaining breakdowns being by way of *K*-capture. The per cent occurrence and the half-lives of each of these three nuclides are presented in Table 1, the values presented being taken or calculated from data appearing in the recent literature.[1, 2, 3]

The human body is, by weight, 0.15 carbon, 0.12 hydrogen, and 0.01 potassium. From this and from the figures given in Table 1, it is possible[4] to calculate the body's natural radioactivity in terms of the number of atoms disintegrating per second (Table 2). Allowing for the *K*-capture variant in the breakdown of K^{40}, the total number of beta particles produced per second in a 70-kg. human body is about 20,000. Of these 85 per cent arise from K^{40} and 15 per cent from C^{14}. The contribution of H^3 is insignificant.

There has been speculation in the past to the effect that beta-radiation from K^{40}, which the body can neither avoid nor escape, is responsible for the development of "spontaneous" cancers. Nahmias[5] has calculated, however, that the effect of the body's K^{40} is to expose each cell of the human body to the formation, on the average, of one ion per year. This effect is of the same order as that produced by cosmic rays and is well below that produced by tolerated doses of short-wave radiation. It would seem then that K^{40} could be eliminated as a significant factor in spontaneous carcinogenesis.

If K^{40} could be so eliminated, it would seem *a fortiori* that C^{14}, which is responsible for less than a fifth of the beta-particle production that K^{40} is, should also be eliminated as a factor. Here, however, there is an important new consideration to be taken into account. In the case of K^{40}, beta-particle production results in a random bombardment of surrounding molecules, with random formation of free radicals or ions. Few of these could be expected, on the grounds of pure chance, to affect the nucleoprotein arbiters of cellular chemistry.

C^{14}, however, can form an integral portion of the organic molecules within the cell including the desoxynucleoprotein molecules that are commonly called genes. A disintegrating C^{14} atom within a gene is not merely the source of a possibly damaging beta particle. That is the least of the affair. In the first place, beta-particle emission converts the carbon atom to N^{14}, altering the chemical nature of the molecule. Secondly, the effect of the recoil after beta-particle emission may well break the covalent bonds by which the carbon (now nitrogen) is attached to the remainder of the molecule. Again the chemical nature of the molecule is altered.

TABLE 1
Radioactive Nuclides Occurring in the Human Body

Nuclide	*Fractional occurrence in element*	*Half-life (seconds)*
K^{40}	1.19×10^{-4}	4.4×10^{16}
C^{14}	1.85×10^{-12}	1.8×10^{11}
H^3	10^{-18}	3.9×10^{8}

Now the content of desoxypentosenucleic acid in individual cells of active tissues is about 6 to 7×10^{-12} grams.[6] Supposing the genes to consist of this plus twice the weight of associated protein, we can put the weight of the genes in a cell at 2×10^{-11} grams. About half of this weight may be taken to be carbon and 1.85×10^{-12} of that to be C^{14}. The weight of C^{14} in the genes of such a cell is therefore just under 2×10^{-23} grams. This means that there is just about one atom of C^{14} present in the genes of an individual cell.

TABLE 2
Radioactivity in a 70-Kg. Human Body

Nuclide	*Grams present*	*Number of atoms present*	*Number of atoms disintegrating per second*
K^{40}	8.3×10^{-2}	1.2×10^{21}	1.9×10^{4}
C^{14}	1.9×10^{-6}	8.1×10^{14}	3.1×10^{3}
H^3	8.4×10^{-15}	1.7×10^{9}	3.0

It can be calculated from this that the number of C^{14} disintegrations in the genes of the human body is about one per year for every 1200 cells. This is only one twelve-hundredth the number of breakdowns Nahmias calculates for K^{40}, yet it is a figure which ought not to be disregarded. Whereas the K^{40} disintegrations

[1] "Handbook of Chemistry and Physics," 35th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1953.
[2] Curran, S. C., *Quart. Revs. (London)*, **8**, 1 (1953).
[3] Hortecк, P., and V. Faltings, *Nature*, **166**, 1109 (1950).
[4] Asimov, I., J. Chem. Educ., **31**, 24 (1954).
[5] Nahmias, M. E., *Cahiers phys.*, **17**, 27 (1943).
[6] Leuchtenberger, C., et al., *Proc. Natl. Acad. Sci. U. S.*, **37**, 33 (1951).

may or may not affect the genes to the extent of inducing mutation, with the chances probably considerably more than 1200 to one against mutagenesis, every one of the C^{14} breakdowns within the gene *must* result in its chemical alteration.

In the light of this, it would be interesting to note whether a diet high in C^{14} would increase the mutation rate in an animal such as *Drosophila* or the rate of tumor formation in cancer-prone strains of mice, and whether any correlation existed between the increase (if any) in mutagenesis or carcinogenesis and the increase (if any) of C^{14} in the genes.

■ ■ ■

AN ACCURACY-DETERMINATION CHART

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In courses in quantitative analysis, students report their results in the percentage present of a certain constituent. The students are usually graded on the basis of the parts per thousand by which they differ in their report from the known value of the sample. Thus, if a student should report 44.22 per cent and the standard unknown analysis of the sample were 44.00 per cent the deviation would be .22 parts in 44.00. To determine the error in parts per thousand, the following calculation is generally performed:

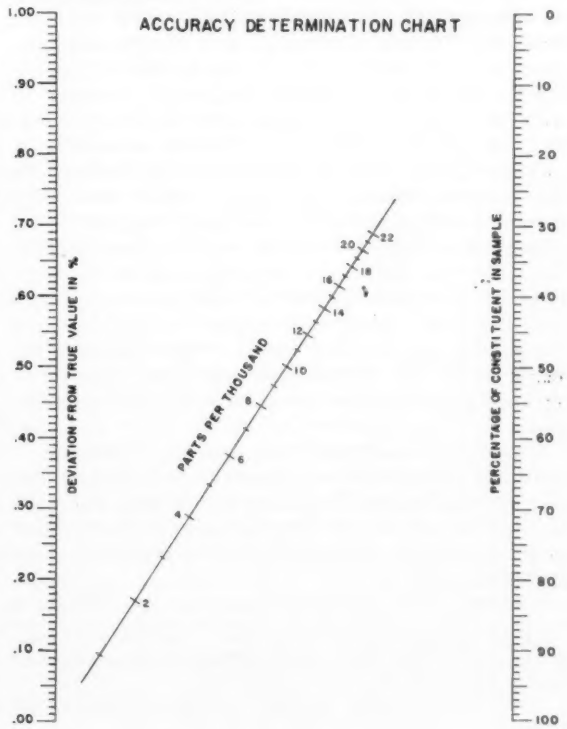
$$\frac{0.22\%}{44\%} = \frac{x}{1000}$$

where x is the deviation in parts per thousand. Grading the reports for a whole class involves a considerable amount of slide-rule calculation and a large chance for error is present, especially in misplacing a decimal point. As the student is usually not told what the true value is for the sample, a slide-rule mistake on the part of the instructor would seriously handicap the student. This danger is eliminated by using the accuracy-determination chart described below, and considerable time is saved.

The chart shows immediately the parts per thousand by which the student varies in his analysis. All one must do to read the chart is to connect the proper marks on the "deviation from true value in %" scale to the "percentage of constituent in sample" scale with a ruler. The intersection of the ruler with the diagonal line in the center gives the parts per thousand directly. Thus, in the example above in which the student reported 44.22 per cent and the true analysis was 44.00 per cent, the difference of 0.22 per cent (on the left hand scale) is connected with 44 per cent (on the right hand scale). The intersection of the ruler with the diagonal line gives the required answer of five parts per thousand. The chart is best read with a transparent plastic ruler. It might also be convenient for the grader to pencil in the grade intervals parallel to the parts per thousand scale: Thus 4–6 parts per thousand would be equivalent to a grade interval of 85, 6–8 parts per thousand to a grade interval of 75, etc.

ACKNOWLEDGMENT

The author wishes to thank Dr. Kuang Lu Cheng for his interest.



CHEMISTRY, CHEMICAL ENGINEERING, AND CULTURE[1]

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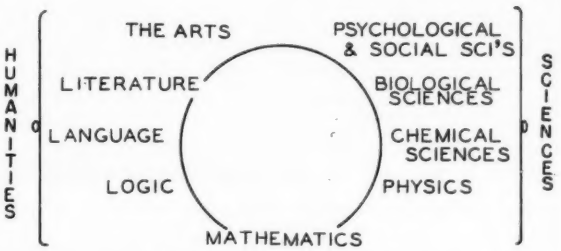
MANY of us, it seems to me, have allowed ourselves to be cowed on the subject of culture. Perhaps we have heard our academic friends exchanging anecdotes about Pepin the Short, or talking about the influence of Charlemagne in dispelling the blackout of the Dark Ages. And because we have understood their language but have not accumulated detailed knowledge of these matters we may have felt at a disadvantage. So let me rehearse some preparatory platitudes: no one can do everything, and no one ever could; our efforts are metered by unyielding time; everyone is a specialist in some way unless he is a total idiot; culture is not a matter of mystery, nor is it something rare, or strange, or quaint, or effete and useless. All productive people contribute to the culture of their society.

But what is culture? The word has many legitimate meanings and countless connotations, some of which have made scientists and engineers unwilling to apply the word to themselves. Perhaps the meaning that comes closest to the intention of this symposium is that which defines culture as the characteristic attainments of a people or social order. We take the further step of defining these attainments as the ideas by which we live[2]—our heritage of ideas in their modern meaning. Now this is an abstract notion, but scientists certainly are not disturbed by abstractness, and we certainly do not need to defend the statement that the abstract ideas that are powerful forces in our society today *are* our culture. These ideas are abstracted by people from the observed behaviors of people. Some have been handed down to us as the wisdom of our ancestors; others are manifestations of the wisdom of our contemporaries. Our culture is sustained, nurtured, conserved, and modified by people in the process of living. It is not static. Many of the people who contribute to our culture may not be cultured in the sense we shall define later, but surely those who contribute to a phenomenon or process should have the right to speak of it.

Returning to our platitudes, since no one can do or learn everything we must all specialize. Yet the fact that we may be specialists does not abrogate our right to speak of culture, for there is no one who is not a specialist who has a better right to that privilege. This is my first point.

Now it is time to become more specific. We have spoken of the culture of our society as a whole, but we cannot here deal with all aspects of this whole. Even if we had unbounded time at our disposal we could still not grasp the rich and changing diversity of our society in any detail—we would still have to deal with abstractions. So in order to become somewhat more specific we must narrow our horizon. We will consider certain aspects of the college and university education, feeling that even in this academic pursuit we will still adhere to a closely correct notion of culture, since our educational system (all of it, of course) transmits our culture to young people.



The Field of Knowledge and Experience

The "sciences" and "humanities" are defined with reference to the various groups of university or college disciplines. Philosophy, religion, ethics, history, and the technologies do not appear in this restricted diagram. To include them would require the introduction of several levels, or other dimensions, into this plane representation. This does not mean that their importance is in any way minimized.

My first point was that we chemists and chemical engineers have as much right to speak of culture, to define, analyze, and criticize, as any other members of our society. My second point bears on the vocational nature of higher education. I have said that we must all be specialists to some degree. This means that our education is, in part at least, vocational. Now I realize that "vocational" is not an "O.K. word," and I am sure we could charm each other with suitably chosen euphemisms; but this is a fact. The existence of major subjects in college supports it, and it is emphasized by the bureaus of vocational guidance which more and more of our colleges are providing in their administrative setups. Let us not delude ourselves about this. We cannot return to some supposed past when those who attended college or university could emerge well versed in all important subjects. That is quite impossible today and I doubt that it was ever possible. Also, let us not be in too much of a hurry to decry the idea of vocational training, as though an

[1] Presented as part of the Symposium on the Cultural Values of Chemistry at the 126th Meeting of the American Chemical Society, New York, September, 1954.

[2] The definition is from ORTEGA Y GASSET, "Mission of the University," Princeton University Press, 1944, p. 81.

expert in the classics were not vocationally trained and a specialist; or an expert in the life and times of Shakespeare were not a specialist. These are honorable specialties, and a good and productive man in these fields ranks equally with a good and productive chemist or engineer. Moreover, let those who would retreat into the past to escape this fact remember that universities were originally organized for vocational purposes, that is, to prepare men for the Church, for law, for medicine, and other public service.

Though we all have to specialize to some extent, our culture is not specialized. It has many aspects which may be classified on the basis of our specialties as humanistic or scientific. In order to define these two classes, the sciences and the humanities, we will consider the broad specialties of the college or university as they are organized and appear in departments or divisions of instruction.

Let us arrange the university disciplines, speaking always in broad terms, in a logical order such as shown in the figure. Here we have devised an arrangement which conveys the idea of relatedness among the disciplines. The domain of knowledge and experience, represented in part by this figure, is a continuum, with divisions in it made only because of necessity imposed by human limitations and the pressure of inelastic time. We extract from the diagram the concept of the sciences and humanities, defining them as shown in the figure, somewhat arbitrarily as in any definition, but meaningfully in terms of present usage.

Our culture consists of the ideas which vitalize these disciplines—which vitalize the field of knowledge and experience. Our culture, this analysis shows, is indisputably *both* scientific and humanistic. Moreover, unless we would slice out sections of this field and discard them as irrelevant, all parts contribute to and complete the whole. People in all disciplines have the right to claim their insights about the whole. They also carry, as justification for this right, the responsibility to try to see that they themselves are not the whole. My second point, then, is an extension of the first. It is that, though we as persons have to specialize, our culture is not specialized, and in claiming our own particular insights we need to recognize that there are other insights. The authority with which we speak of culture increases, it seems to me, as we gain in that wisdom that harmonizes the scientific with the humanistic aspects of our culture.

My third point is neither a platitude nor a new idea. This is that the profession of chemical engineering is more humanistic, basically, than that of chemistry, and in general that the engineer and professional technologist (and I include here the lawyer and the physician) are in an unusually strategic position to mediate between the humanities and the sciences. Let me support this point with the following evidence.

It is often claimed that a distinguishing mark of the humanist is his preoccupation with the individual work in literature, or art, while the scientist seeks the general law, excluding the peculiarities of the individual for the sake of the generalization that he seeks. This is true enough (within limits). But the engineer takes these general laws and applies them to produce an individual work which may be a refinery, or a bridge, or some other structure, in each case returning from the general, statistical law, to the individual exigencies of its application. Here all those aspects of individuality, the modifications to fit the location, to fit the particular use, and so on, must be met.

Take another bit of evidence. The technologist, in applying science, must make judgments which are basically ethical or moral. Consider not only the physician, or lawyer, whose need to make ethical judgments is plain to be seen, but even the chemical engineer. In designing a refinery nowadays, how often must he weigh the question of responsibility to the public—in the elimination of smoke, in the disposal of waste, in the design of an elegant structure? If you reply that these judgments are assisted by regulative laws, I would continue my evidence by citing the codes of ethics that these professional men have developed, not forgetting when I cite the physician's Aesculapian oath to cite as comparable to it the code of the professional engineers in their responsibility to the public. Yet it is just in the realm of value judgments that the humanist often finds a distinguishing difference between himself and the scientist. I do not wish to pursue this further, but I wish to leave the thought with you that in his service to the public, in applying to the individual instance the more general and theoretical laws of the sciences (and humanities) the technologist is in many ways a mediator between the humanities and the sciences, and in many ways is in closer touch with our culture than are the others.[3] It should not be forgotten, too, that the humanities have their technologies.

So far, we have emphasized differences. My fourth point bears on similarities. It is that at a very fundamental level all productive members of our society—all those who actively maintain, and who generate, so to speak, our culture—are doing the same kinds of things even though they may speak of them in different words. This is partly because all our variety of specializations have a common basis and common purposes: the basis, a common heritage; the purposes, those of the pursuit of knowledge and experience. Let us consider three explicit cases.

In the area of creative activity the humanist and scientist speak essentially the same language. This is the activity in which the human being produces, by some subtle alchemy, something great that was not in existence before. It might be a new theory that brings together what once were thought to be disparate facts, and predicts somethings not previously evident. It might be a great literary work that shows what human beings can be in distinction to animal-kind. It might be a work of art, or an entire movement in some field. In such creative work there is between humanist and scientist a brotherhood in travail—in experiment, test-

[3] See MOBERLY, SIR WALTER, "The Crisis in the University," SCM Press, Ltd., London, 1949, pp. 43–4.

ing, rejecting, judging—that removes any distinction that the more practical level of ordinary activities imposes. If you think of this I feel that you will agree with me in general.

Again, experimentation is often considered to be a scientific characteristic that is not developed to nearly so high a degree of effectiveness by the humanist. Here is the finest definition of experiment I have ever seen: "By experiment I mean an investigation that is supported by prior knowledge, based upon a hypothesis, conducted with intelligent reason, and carried out in the realm of technique." This definition was given by a critic of art, Professor Henri Focillon. He goes on to say, in his discussion of the development of Gothic architecture, that "The proof of its experimental character is the fact that, in spite of the rigorousness of its methods, some of its experiments remained almost wholly without results; in other words, much was wasted, much was barren . . . How little do we know of the innumerable mistakes that lurk in the shadow of success!"[4] Do not these two passages ring true to the ears of the productive scientist?

I am sure that many of you have felt, in mastering a difficult technique, in producing a beautifully crystalline substance, or in contriving some new and elegant experiment, quite the same kind of thrill that a writer, artist, or musician might feel in the corresponding circumstances in his own field. These are human matters, and scientists and humanists are not different species of human beings—as some extremists seem to suggest.

My last point has to do with what makes the cultured person. Perhaps we might say that a cultured person is one who comprehends the great ideas of his time in perspective against those of the past; one who understands the power of ideas and has made out of this knowledge of these ideas the choices that guide his behavior. I think that we can describe a cultured person somewhat more specifically by saying that today he must understand rather deeply what science tries to do and how it tries to do it, and he must be aware, at least in a general way, of the strengths and weaknesses of science. He must also, and with equal necessity, know the distinguishing characteristics of the humanistic approaches to knowledge and experience and their strengths and weaknesses. He will be a specialist in one area of the sciences or humanities, but his claim to being cultured will be strengthened in proportion to his success in the creative combination of his knowledge of the two areas.

The question may legitimately be asked how close we are in actuality to this ideal of culture. Here I must tread softly! It seems to me that the danger of being uncultured nowadays is greater among humanists than among scientists. I am not saying this to disparage the humanist, for I think the problem for him is much more serious than for the scientist. How many mathematicians, physicists, biologists, that we ourselves know carry on some activity in music, art, literature, or other humanistic enterprise; but how few humanistic specialists also pursue science? You will, I am sure, agree that it is much easier for a good scientist to be a middling musician or artist, than for a good musician to be a middling scientist.

This is in part because of the great problem of language. The mathematical and other scientific languages place a substantial barrier before the humanist. On the other hand the language of the humanist is English, (or perhaps French or German or Latin) or music, and so on, to which the scientist has been exposed right along. This is a difficulty which we must recognize and help to remove. We cannot retire into an elevated holier-than-thou attitude, saying, as I have heard one or two scientists remark, that scientists don't have any trouble with history and literature, and if humanists have trouble with physics and chemistry it's their own fault. It is our fault too, and it is increasingly recognized as our responsibility. We must make the gift of our scientific insights more available and more attractive to the humanist.

A curious result of this difficulty for the humanist to become a fairly knowing scientist, while the scientist can in general much more easily become a pretty good humanist, is that the sense of "crisis in the university" is greater among humanists than among scientists.

I have tried in this brief and hurried survey to say many things without adequate supporting evidence, and I am sure that many details could be argued. But in my main points, at least, I have tried to bring together some things that most of you will have already thought of. We as chemists and chemical engineers have as firmly based a right as anyone else to speak of culture—to evaluate and criticize. We have this right because we are active participants in creating and nourishing our culture. Furthermore, the fact that we are specialists and are vocationally trained is a necessary feature of our ability to contribute to culture and of our claims to being cultured. It is only if we are merely specialists and one-sidedly and exclusively narrow that we forefeit our right to be called cultured; for all men are specialists to some extent. It seems, too, that the engineer or technologist who carries scientific theory to the everyday world of practice is in a particularly favorable position to develop in himself and his colleagues and students a high degree of culture. This is because he must (or should) learn the language of the sciences and also that of the humanities, even though this latter may be disguised under very practical names. Finally, I have pointed out that when he is engaged in creative acts, whether building a great and living industry or producing an elegant synthesis or equation, the chemist or engineer is doing the same kind of thing in much the same way that the artist or creative humanist is, even though his materials, detailed language, and objectives may be somewhat different; at this level, at least, there exists a unity that can perhaps be constructively utilized.

[4] FOCILLON, HENRI, "The Life of Forms in Art," Wittenborn Schultz, Inc., New York, 1948, p. 9.

THE LAWS OF DEFINITE COMPOSITION AND OF MULTIPLE PROPORTIONS: A GRAPHICAL APPROACH[1]

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TRAINED chemists frequently find it a tedious task to teach the fundamental laws of the kinetic-molecular hypothesis. Some rely heavily on the fund of high-school chemistry that the freshman has carried into college. Many begrudge the time spent on such topics, for which the rest of the syllabus will provide inductive confirmation. Thus the qualities of clear teaching and distinct comprehension are apt to suffer in this part of the course. The remedy, here proposed, may be attractive.

The proposal is a graphical method for teaching the laws of definite composition and of multiple proportions. In this method numerous arithmetical operations are minimized so that fuller meaning of the laws themselves can be realized. The method provides a copious choice of data, from which the most striking may be selected. At an early date in the course the student is introduced to linear mathematical relationships such as he will encounter generally throughout the rest of it. Efficiency in teaching these topics is further provided from the point of view that time and effort are saved for instructor and student alike.

The law of definite composition states that in every pure compound the ratios of the weights of the elements have a constant value (see the table, columns 1, 4, and 8). Limiting our illustration to a compound of two elements, such as nitrogen and oxygen in nitrous oxide, the ratio of the weight of oxygen to that of nitrogen, 0.571, is the constant value for all samples of the pure compound. This can be shown graphically, as in the figure, by plotting a given weight of nitrogen in nitrous oxide against its corresponding weight of oxygen. Since most students come to the course with a clear but popular idea of what analysis implies, quantitative data can be used. It is then convenient in practice to plot the percentage of one element against that of the other, as grams per hundred grams, and to draw a straight line through this point and the origin. One invokes numerous other analyses, expressed in weight ratios, to justify the straight line. The constancy of these ratios is then shown from the graph and possibly confirmed on a dem-

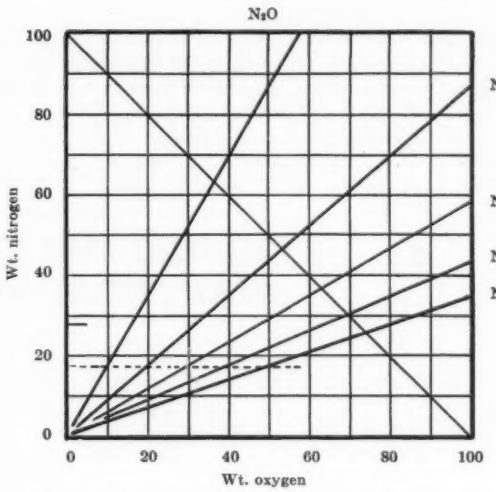

Illustration of the Laws of Definite Composition and of Multiple Proportions in the Oxides of Nitrogen

[1] From a paper presented before the New England Association of Chemistry Teachers at Emmanuel College, Boston, Mass., May 15, 1954.

(1) *Substance*	(2) *%N*	(3) *%O*	(4) W_O/W_N, *g.*	(5) $W_O/17.5$ *g. N*	(6) $W_O/28.0$ *g. N*	(7) *Integral relationship*	(8) *Known formula*
Nitrous oxide	63.7	36.3	0.571	10	16	1	N_2O
Nitric oxide	46.7	53.3	1.142	20	32	2	NO
Nitrogen trioxide	36.9	63.1	1.713	30	48	3	N_2O_3
Nitrogen tetroxide or dioxide	30.4	69.6	2.284	40	64	4	NO_2 or N_2O_4
Nitrogen pentoxide	25.9	74.1	2.856	50	80	5	N_2O_5

onstration slide rule. Such compounds are then compared and contrasted with mixtures.

Other compounds of nitrogen and oxygen are similarly graphed and a family of such curves is obtained. In the figure, note that the points at the intersections of the definite-composition curves with the diagonal line running from upper left to lower right show the percentage composition of the respective compounds. At any point along this diagonal the two percentages add up to 100. This is of help in plotting the points, in checking their accuracy, and in picking off percentage-composition values once the graph is made (see columns 2 and 3 in the table).

This family of curves is used in teaching the law of multiple proportions. Inspection of the graph shows very readily that at a value of 17.5 g. nitrogen, the values of oxygen run 10 g. in nitrous oxide and by stages of 10 g. to 50 g. in nitrogen pentoxide, along the dotted horizontal line in the figure, and as listed in column 5 of the table. Thus, we have two or more compounds of the same elements, such that to a fixed weight of one of the elements (nitrogen), the weights of the other element (oxygen) in each of the compounds are to each other in the ratio of integral numbers (1 to 5, respectively, in the table, column 7). This is essentially the law of multiple proportions—easier to illustrate than to enunciate. One can then verify the law for more familiar data, such as for 28 g. of nitrogen (the table, column 6).

Graphical verification of the inverse problem, which involves a fixed weight of oxygen, is obscure by this method; but obscurity does not invalidate the law.

FINDING THE REST POINT OF AN UNDAMPED ANALYTICAL BALANCE[1]

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In most textbooks on quantitative analysis, instructions for finding the rest point of an analytical balance are presented without explanation. The student is told to allow the beam of the balance to swing freely and to take three or five consecutive readings of the extremes of the oscillations. The point midway between the left- and right-hand averages is taken as the rest point. Of the two derivations of the method to which reference is sometimes made, neither is completely satisfactory. A mathematically exact method for finding the rest point from three readings is possible. The two usual derivations, together with the more exact one, are presented below.

One proof[3] depends upon the assumption that the amplitude of each swing is less than the preceding one by a constant amount k. According to Swift, if the first turning point of the pointer is b divisions away from the actual rest point (the position of the pointer after a very long time), then the next turning point is $b-k$ divisions away, the third $b-2k$, and so on, as shown in Figure 1. The average of the first two readings on the left is $b-k$ divisions to the left of the rest point and the first reading on the right is the same number of divisions to the right. For a total of five readings, the average of the three on the left is $b-2k$ divisions to the left of the rest point while the two readings on the right give an average which is $b-2k$ divisions to the right of the rest point. In each case, the point midway between the left and right averages is the rest point. Although the result is the desired one, and is valid with negligible error for a good analytical balance, the assumption of a constant decrement implies that after a finite number of swings the pointer will suddenly come to rest.

The other proof sometimes referred to[4] assumes damped harmonic motion of the beam, *i. e.*, the

[1] Presented before the Division of Chemical Education at the 126th Meeting of the American Chemical Society, New York, September, 1954.

[2] Present address: RCA Victor Division, Radio Corporation of America, Harrison, New Jersey.

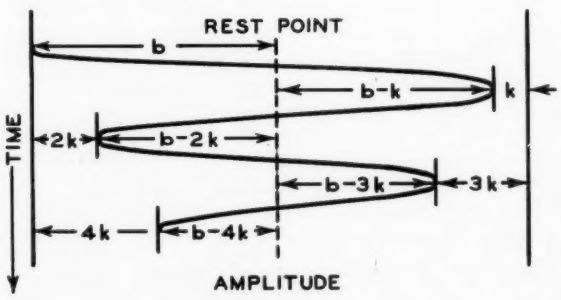

Figure 1

[3] Swift, E. H., "Introductory Quantitative Analysis," Prentice-Hall, Inc., New York, 1950, p. 18.

[4] Fales, H. A., and F. Kenny, "Inorganic Quantitative Analysis," Appleton-Century-Crofts, Inc., New York, 1939, pp. 678–80.

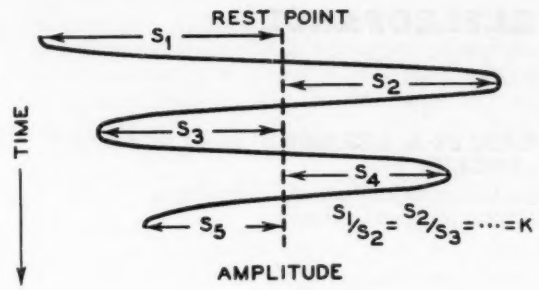

Figure 2

amplitudes of the vibrations of the balance pointer decrease by a constant factor, so that

$$\frac{S_1}{S_2} = \frac{S_2}{S_3} = \ldots = K$$

(see Figure 2). According to the method of proof and the nomenclature used by Fales and Kenny, this constant is characteristic of the balance, and is equal to $e^{aT/2}$, where e is the base of the natural logarithms, a is related to the coefficient of friction, and T is the period of vibration in seconds. Usually, for a good analytical balance, a is very small, so that the quantity $aT/2$ is also small, say 0.1, whence the constant $e^{aT/2}$ is slightly greater than unity ($e^{0.1} = 1.10$).

Expanding the constant gives

$$e^{aT/2} = 1 + \frac{aT}{2} + \frac{(aT)^2}{8} + \ldots$$

Only the first two terms $\left(1 + \frac{aT}{2}\right)$ are considered. It follows that

$$S_3 = S_3$$
$$S_2 = S_3\left(1 + \frac{aT}{2}\right)$$
$$S_1 = S_3\left(1 + \frac{aT}{2}\right)^2$$

The average of the two amplitudes on the left is

$$\frac{S_1 + S_2}{2} = \frac{S_3}{2}\left(1 + \frac{2aT}{2} + \left(\frac{aT}{2}\right)^2\right) + \frac{S_3}{2}$$

If the squared term (small compared with unity) is neglected, then this average is the same as S_2, the amplitude on the right. Thus, to a first order of approximation, the rest point lies halfway between the average of the two readings on the left and the one on the right. (A similar result holds for five readings if terms in $aT/2$ of degree higher than the first are neglected.)

Expanding $e^{aT/2}$ and considering only the first two terms of the expansion, as Fales and Kenny do, implies the introduction of an error. However, the introduction of the exponential is completely unnecessary. For a good balance the constant K is slightly greater than unity, say $(1 + x)$ exactly. The rest of the proof would be as before, the only error being due to the omission of squared and higher terms in x.

The two proofs presented above involve errors which are small for good analytical balances, but starting with the same assumption of damped oscillations, a method of calculating the rest point without computing error is possible. If the constant ratio of amplitudes

$$\frac{S_2}{S_1} = \frac{S_3}{S_2} = \frac{S_4}{S_3} = \ldots$$

is r (the reciprocal of the K used by Fales and Kenny and less than unity), then the number of scale divisions between consecutive readings of the pointer will also decrease by the same factor, *e. g.*,

$$\frac{S_2 + S_3}{S_1 + S_2} = \frac{S_1 r + S_1 r^2}{S_1 + S_1 r} = r$$

It can be seen from Figure 3 that if the initial reading on the left is c (negative if the first turning point is to the left of the balance scale zero), and the first swing takes the pointer d scale divisions to the right ($S_1 + S_2$ in the notation of Fales and Kenny), the second reading will be $c + d$, the next $c + d - dr$, then $c + d - dr + dr^2$, and so on. The true rest point is c plus the sum of the infinite geometric series:

$$d - dr + dr^2 - dr^3 + \ldots$$

having the common ratio $-r$, or

$$c + \frac{d}{1 + r}$$

exactly. For example, the three readings 5.1, 15.7, 5.4 give the rest point

$$5.1 + \frac{15.7 - 5.1}{1 + \frac{10.3}{10.6}} = 5.1 + 5.4 = 10.5$$

Of course, if the balance scale zero were shifted, the values of d and r would be unaffected but the reading c would be different and the new calculated rest point would be shifted by the same number of scale divisions as the scale zero.

Ordinarily, finding an arithmetic mean is simpler than calculating the formula given above, and the difference between the results of the two methods of computing rest points is insignificant for values of r close to unity (less than 0.05 divisions for initial readings 30 divisions apart at $r = 0.90$). However, it is interesting to note that there is a mathematically exact method for finding the rest point of an analytical balance from only three readings.

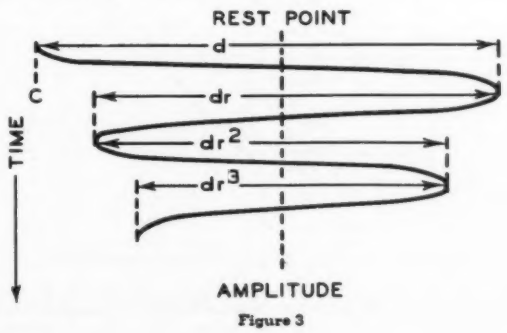

Figure 3

EXPERIMENT ON REFLECTANCE MEASUREMENTS

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Massachusetts Institute of Technology, Cambridge, Massachusetts

THE chemist has long been familiar with the characterization and determination of dissolved substances by means of their absorption spectra. Relatively few, however, have had experience with reflectance measurements unless familiar with the textile, paint, or ceramic industries where reflectance is used routinely to characterize colored solids. In these industries it has been recognized that the nature of the surface plays fully as important a part in the appearance of the sample as the chemical composition. For example, a polished section of didymium glass appears moderately pink by transmitted light, the exact color depending upon the angles of illumination and viewing. That same section of glass, after sandblasting or etching, has a distinct whitish cast; powdered didymium glass is only faintly pink. In each case, however, the sample would have the same chemical composition. The physicist has been concerned with the problem of defining objectively the appearance of colored solids by reflectance, taking into account the physiological and psychological factors that are involved when, for example, a person thinks one piece of cloth is "redder than another." An excellent discussion of the subject can be found in the recent book by Judd (*1*).

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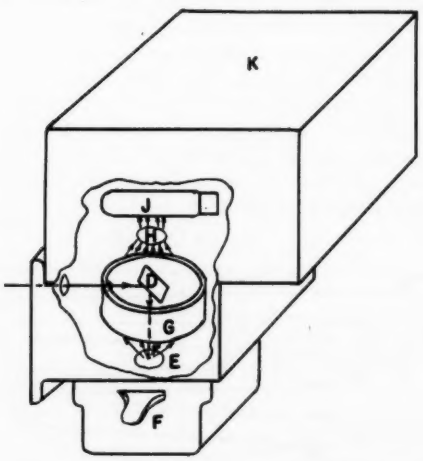

Figure 1. Cut-away View of Reflectance Attachment

D, Reflecting 45° mirror; *E*, Exposed surface of sample; *F*, Sample drawer; *G*, Mirror for collecting light reflected from the sample at 35–55°; *H*, Frosted quartz "diffuser plate"; *J*, Photomultiplier tube; *K*, Housing.

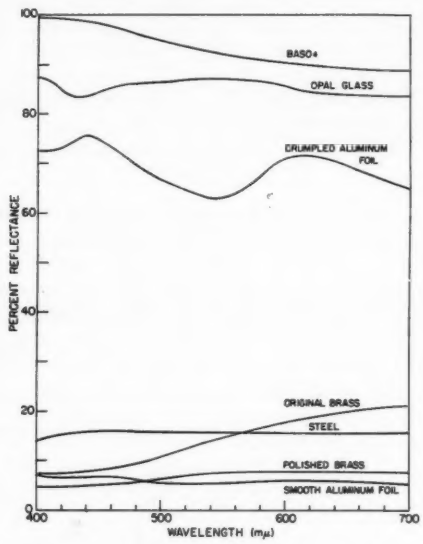

Figure 2. Typical Reflectance Curves for Substances Measured against Magnesium Carbonate

The fact that the nature of the surface makes an important contribution to the appearance of a sample means that the reflectance spectrum will also be gravely affected. Hence, one would expect the chemist to restrict the application of reflectance, as a measure of composition, to those cases where the surfaces of the samples were very nearly alike. An obvious application that fulfills this requirement is the identification and determination of substances on paper chromatograms. An analogous problem that has been handled is the determination of the amount of soil in fabrics (*2*). Similarly, the amount of carbon impurity in different samples from a large lot of powdered catalyst is amenable to determination by reflectance measurement (*3*). Thus, because it appears that reflectance will become increasingly useful to the chemist, an experiment was devised two years ago for inclusion in a course on instrumental analysis. The highlights are being reported here as a guide for others who may wish to set up a similar experiment.

MEASURING TECHNIQUE

Although reflectance instruments employing filters for isolating different portions of the spectrum are commercially available, the use of a spectrophotometer is advantageous just as it is in making absorbance

measurements. A standard diffuse-reflectance attachment for the Beckman Model DU spectrophotometer, shown schematically in Figure 1, was used, although the Beckman Model B and its reflectance accessory should be equally satisfactory. In using the Model DU, a photomultiplier attachment was found to be advantageous because only a small fraction of the original light is collected for measurement.

The primary reflectance standard against which absolute measurements should be made is a freshly formed layer of magnesium oxide produced from a burned ribbon of magnesium. However, magnesium carbonate, which can be purchased in the form of 1-in. × 2-in. × 3-in. blocks from many druggists, serves admirably after the surface has been scraped carefully with the flat edge of a spatula. Polished opal glass is the most practical reference, though as shown in Figure 2, its reflectance is noticeably less than that of magnesium carbonate. For the sake of comparison, the reflectance of a sample of pure barium sulfate, pressed flat before measurement, is also shown. In contrast to the high values for white substances are the reflectances of about 1 per cent for polished black glass and 3 per cent for a black cloth. When measuring cloths, several thicknesses should be used in order to minimize reflectance from the background.

TYPICAL PROCEDURES

The first procedure, designed to show the similarity in absorbance data and those of reflectance, consists of measuring the absorption spectrum by regular transmittance measurements and by means of the reflectance attachment. A simple cut-off filter or didymium glass may be run, the latter being much more time-consuming. It is worth while to note the difference between the transmittance spectra obtained when using an air blank as compared to one of clear glass. Similarly, the transmittance spectra obtained by reflectance may be compared, using either an opal glass by itself or one covered with a clear glass (Figure 3). Owing to variations between the blanks, spectra obtained by regular transmittance cannot be related in a simple way with those obtained by the reflectance technique.

Progressing to "true" reflectance measurements on opaque media, the student is usually quite surprised to discover how low the reflectance of shiny aluminum foil can be. If the foil is then crumpled, more or less flattened by stretching gently, and again measured, its diffuse reflectance is increased many-fold (Figure 2). The resulting increase in reflectance is visible to the eye under an incandescent light as an increase in "whiteness" similar to that observed upon etching the polished face of a glass filter.

Figure 2 also shows typical reflectance curves from polished samples of brass and steel. The color of brass, which is readily apparent to the eye, is seen to be the result of a gentle slope toward slightly less reflectance at shorter wave lengths. Once again, one may illustrate the effect of surface roughness by comparing the curves for a brass sample before and after being highly polished.

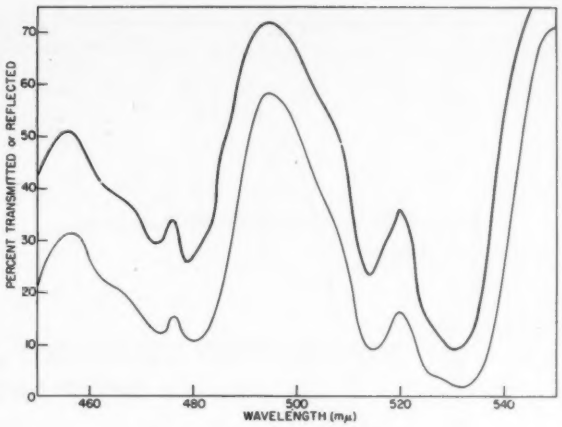

Figure 3. Polished Didymium Glass

Upper curve: Conventional transmittance technique using an air blank. *Lower curve:* Reflectance technique using opal glass as a standard and as a backing for the didymium sample.

Relationships between reflectance and concentration, which are of more direct interest to an analytical chemist, can be shown in a number of ways. Mixtures of barium sulfate with ferric oxide or cupric oxide in the range up to about 20 per cent (by weight) of the colored components have been prepared with little difficulty. One should run each sample through a 100-mesh screen twice, to insure complete mixing. Unless the number of screenings is held constant, the samples may show larger variations than otherwise.

After obtaining the reflectance spectrum for one

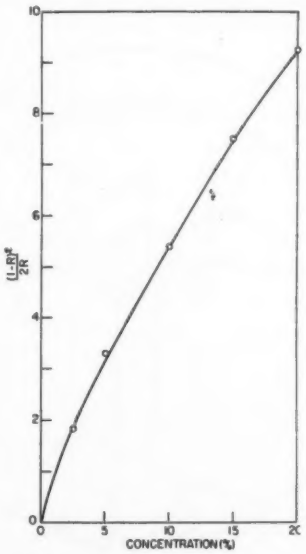

Figure 4. Kubelka-Munk Plot of Data from Samples of Cloth Dyed with Brown BN

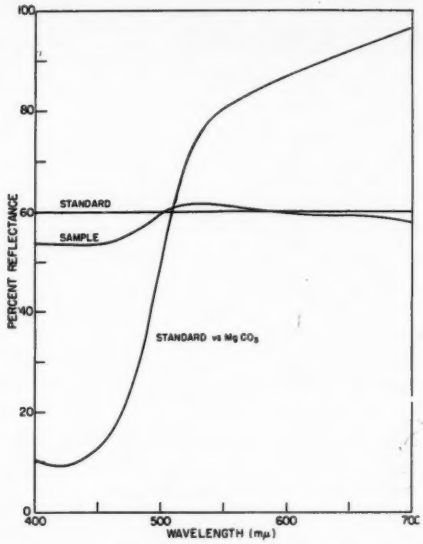

Figure 5. Differential Data for the Comparison of Cloths Dyed with Two Preparations of Ponsol Brown ARD. The Sample Had Previously Been Judged Visually to Be "Weaker and Duller" than the Standard

of the samples, the remainder need be measured at only one wave length. Although the resulting data may be plotted in a number of ways, the Kubelka-Munk relationship is the one most frequently employed, and is often linear over only a small concentration range. The concentration is plotted against $(1 - R)^2/2R$ where R is the reflectance. A table of values for this function is included in most books dealing with reflectance, including the one by Judd (*1*). Figure 4

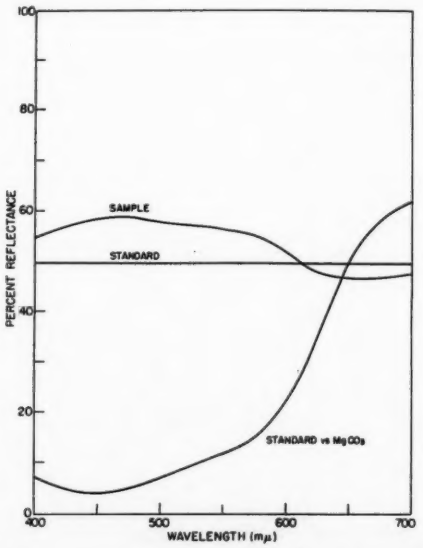

Figure 6. Differential Data for the Comparison of Cloths Dyed with Flavone GC Paste. The Sample Had Previously Been Judged Visually to Be "Greener and Somewhat Brighter" than the Standard

shows such a plot for a number of cotton cloths printed with different concentrations of dye (Ponsol Brown BN). From work done in the authors' laboratory, it appears that reflectance values of a sample, after subtraction of the reflectance for the pure dye or pigment, will fall on a straight line when plotted as the logarithm against $\sqrt{C}$ or against $\sqrt{C/(1 - C)}$, where C is the concentration of the colored substance in the sample (*4*).

Though it has not been included in an experiment, the use of differential reflectance measurements to increase the precision with which small differences in reflectance can be measured can be performed (*4*) in a manner strictly analogous to that proposed by Hiskey (*5*) and by Bastian (*6*). The resulting differential curves also provide results which can be readily interpreted by persons interested in comparing the "closeness-of-match" of two pieces of dyed cloth. Typical comparisons are shown in Figures 5 and 6, together with the results of a visual comparison. The standard in each case was set at an arbitrary value of less than 100 per cent reflectance so that regions of the spectrum which reflected more than the standard could be measured easily. For those not familiar with the terminology, "dullness" usually results from the the presence of either a neutral gray substance or the complementary color. "Brightness" may be due either to greater reflectance in the yellow-green portion of the spectrum or to "weakness," a lower concentration of the colorant and hence greater reflectance in the region of maximum absorption.

DISCUSSION

It would appear that the potentialities of reflectance deserve more attention from the chemist, particularly the analytical chemist. Reflectance should permit many analyses to be made directly upon solids, thereby facilitating the analyses of difficultly soluble materials. In order to obtain maximum precision, it will be necessary to minimize variations due to differences in surface roughness, including particle-size distributions of powdered samples as a special case of surface roughness. Analyses of precipitates may demand special care to meet this demand.

The physical chemist can also use reflectance to advantage in determining the structures of solids, including glasses (*7*, *8*).

ACKNOWLEDGMENT

The authors are grateful to Dr. W. R. Waldron, of the Chambers Works of E. I. du Pont de Nemours and Co., for supplying the samples of dyed cloths and the color judgments with which the spectrophotometric results were compared.

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CIRCULAR-PAPER CHROMATOGRAPHY IN QUALITATIVE ANALYSIS

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PAPER chromatography, as developed by Consden, Gordon, and Martin (*1*) in 1944, has undergone many modifications and has been utilized in the analysis of many diversified mixtures. The introduction of the circular-paper chromatographic technique of Brown (*2*), a distinct phase of paper chromatography, has proved to be a very convenient and versatile analytical tool. This relatively new technique possesses several advantages over the conventional methods of paper chromatrographic analysis.

In general, the method has a greater sensitivity, resolving power, and reproducibility. In view of these facts, very exact quantitative determinations can be carried out. The apparatus, because of its compact nature, can be stored readily in an oven or refrigerator when temperature control is necessary. Its greatest advantage, however, lies in the relatively short time of development of a chromatogram.

Some of the features which differentiate circular-paper chromatography from linear methods are the following: the components are resolved in circular zones, a central feed technique is employed, and the solvent flow is in a horizontal direction. For this reason it has been referred to by many as the horizontal migration method.

Although much work has been accomplished with circular-paper chromatography in the analysis of amino acids, sugars, etc., only a slight fraction of the reported literature has been devoted to inorganic procedures.

Rutter (*3*), who generally is credited with the method of horizontal migration, was the first to apply this technique to the separation of inorganic ions. Pollard and McOmie (*4*), as well as Martin (*5*), used the preceding technique in reporting the Rf values of a number of common cations. This same scheme was used for the qualitative and quantitative determination of copper, iron, nickel, and zinc in aluminum alloys (*6*). Methods have also been reported for the separation of cobalt, nickel, and copper (*7*), and radium D, E, and F (*8*), using the horizontal migration method of Rao and Beri (*9*).

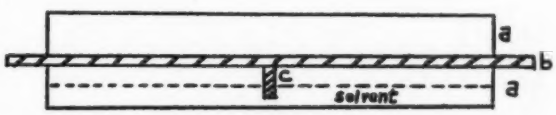

Figure 1. Arrangement for Circular-Paper Chromatography

a, Petri dish. *b*, circular filter paper. *c*, wick immersed in solvent.

Since the movement of the solute goes both in the

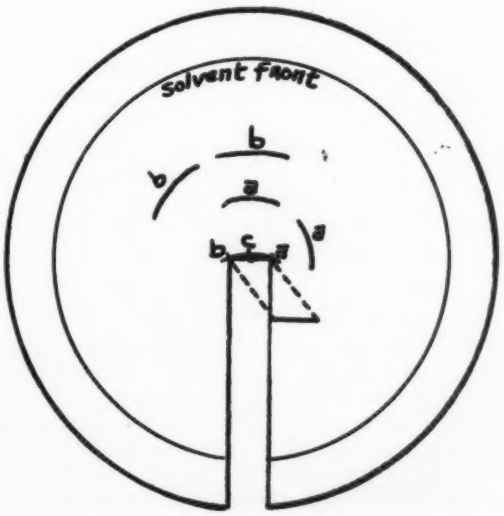

Figure 2. Modified Rutter Technique

a, *b*, unknown solutions. *c*, known solution of *a* and *b*.

TABLE 1

Group I (Silver Group)

Type of paper: Whatman No. 1
Time: 0.5–0.75 hour
Solvent: 40% tertiary butyl alcohol, 40% acetone, 12% water, 8% conc. nitric acid

Cation	*Identifying reagent*	*Color*	*Rfc*
Ag^{+}	H_2S	black	0.25
Hg_2^{++}	"	black	0.00
Hg^{++}	"	tan	0.81
Pb^{++}	"	brown	0.50

Group II (Copper Group)

Type of paper: Whatman No. 1
Time: 0.5–0.75 hour
Solvent: 40% tertiary butyl alcohol, 40% acetone, 11% water, 4.5% nitric acid (6 *N*), 4.5% acetyl acetone

Cation	*Identifying reagent*	*Color*	*Rfc*
Pb^{++}	H_2S	black	0.15
Cd^{++}	"	yellow	0.32
Cu^{++}	"	dark brown	0.40
Bi^{3+}	"	brown	0.76
Hg^{++}	"	tan	0.90

Group IIB (Arsenic Group)

Type of paper: Whatman No. 1
Time: 0.5–0.75 hour
Solvent: 45% tertiary butyl alcohol, 45% chloroform, 8% hydrochloric acid (8 *N*), 2% acetyl acetone

Cation	*Identifying reagent*	*Color*	*Rfc*
Sb^{3+}	dithizone	red-orange	0.85
As^{3+}	"	yellow	0.64
Sn^{++}	"	purple	1.00

direction of the flow of the solvent toward the edge of the paper and also in the direction orthogonal to the direction of flow of the solvent, circular-paper chromatography has been considered by some to be a two-dimensional phenomenon (*10*). In fact, it is the two-dimensional movement which is responsible for the higher Rf values obtained in circular-paper chromatography as opposed to linear-paper chromatography. For this reason it has been suggested that the Rf values obtained by the horizontal migration method be referred to as circular Rf values (*9*). The authors are in favor of such a suggestion and propose the symbol Rfc, which is defined thus:

$$\text{Rfc} = \frac{\text{distance from the initial spot to center of each zone}}{\text{distance from the initial spot to the solvent front}}$$

In circular-paper chromatography, identification of the unknowns can be accomplished either by measuring the circular Rf values (Rfc) or by the technique of mixed chromatograms (*11*), which permits the identification of the unknown by reference to the known run on the same chromatogram. The latter method is recommended for student use in qualitative analysis because of its simplicity. Rf values are dependent upon temperature, pH, solvent system, time of development, humidity, etc.; and these specified conditions must be fulfilled for direct comparison with published Rf values (*12, 13, 14*).

Circular Rf values decrease with an increase in the distance of the initial spot from the center of the filter paper, or stated in another way, with an increase in the length of the tail (*12, 15*). Accordingly, the variation of the length of the wick can significantly alter the mode of separation of mixtures. For example, an increase in the length of the wick made possible the separation of manganese from nickel using tertiary butyl alcohol and concentrated hydrochloric acid (7:3) as the developing solvent. This is assumed to result from the preferential adsorption of acid and/or water by the paper, thus gradually resulting in a change in the composition of the developing solvent and consequently a change in the Rfc values.

A change in concentration of the solute does not alter the Rfc values if the measurements are made to the "center of gravity" of the zone. An increase of concentration, however, though not affecting Rfc values directly, may nevertheless cause overlapping of the zones and result in incomplete separation. The overlapping in this case is due to an increase in the diffusion of the zones which accompanies an increase in concentration. It may be noted here that for separation to occur between two solutes the difference in Rfc values should be greater than 0.06 (*16*).

The relationship between the width of the wick and the rate of flow of the solvent has also been determined (*17*). As would be expected, an increase in the width of the wick will cause a proportional increase in the rate of flow of the solvent with no change in Rfc values. Thus, variation of the wick width can serve to increase the distance with which a solvent moves in a given time.

The diameter of the filter paper plays a predominant part in the resolution of mixtures. Circular filter paper varies in size from 11 to 35 cm. in diameter. The use of large filter paper is found to be advantageous for better resolution and increased accuracy in the Rfc measurements (*18, 19*). However, for student work, satisfactory results are obtained with filter paper as small as 11.5 cm.

PROCEDURE

The method of chromatographic analysis employed by the authors is a modification of the Rao and Dickey method (*16*) for the direct positional comparison of unknown substances. The apparatus consists of two Petri dishes of the same diameter, a capillary pipet, Whatman No. 1 and No. 2 circular filter paper (11.5 cm. in diameter), and the developing solvent. A diagram of the apparatus is illustrated in Figure 1.

The procedure is as follows: A chromatogram is prepared according to the method of Rutter (*3*). A 120° arc of a circle of 4-cm. radius is drawn in such a way that the edge of the wick forms a chord of the circle (see Figure 2). The samples of the unknown to be analyzed are placed at each corner of the wick and the known in the center of the arc segment. The paper is dried and placed over a Petri dish in such a way that the

tail is immersed in the developing solvent (10 ml.) contained within the dish. The paper is then covered with another Petri dish of the same diameter in order to control the atmosphere surrounding the chromatogram. After development the chromatogram is dried and treated with a suitable chromogenic reagent to reveal the location of the ions. Development of the paper results in the formation of three arcs separated from one another by a distance of one to two millimeters. Identification of the unknowns can be accomplished by the direct comparison of the outer zones to the central zone.

SEPARATION OF GROUPS I AND II CATIONS

The silver and copper groups can be conveniently identified by means of an aqueous solution of hydrogen sulfide. The corresponding colors of the sulfides are listed in Table 1. It should be noted that since silver sulfide is soluble in an acid medium the chromatogram must first be neutralized with ammonia or else

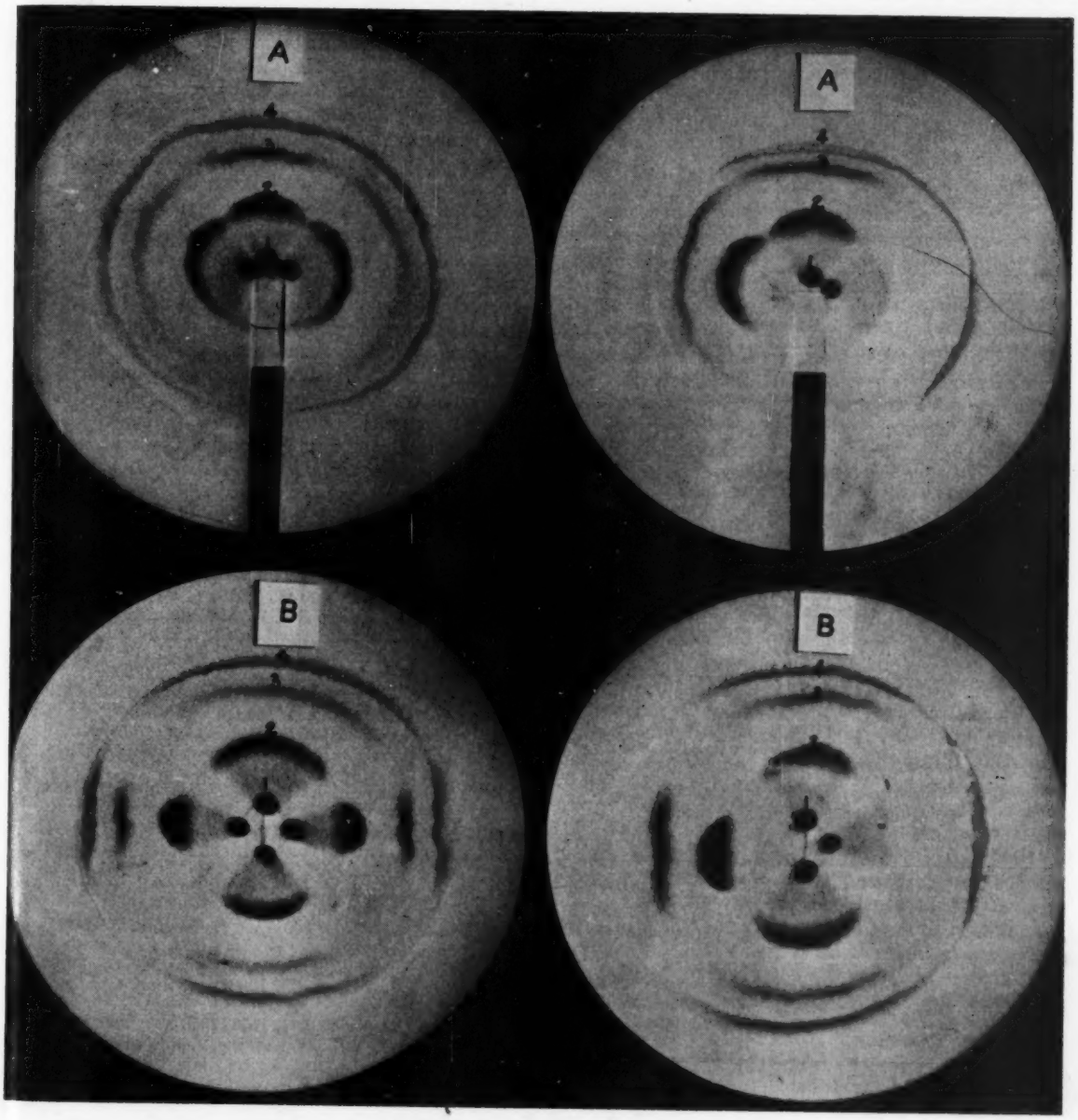

Figure 3. Separation of the Copper Group

A, modified Rutter technique. *B*, Giri method. 1, lead. 2, copper. 3, bismuth. 4, mercury.

the silver will fade when the chromatogram is dried.

Members of the arsenic group should be permitted to dry thoroughly in air for at least 15 minutes before development. The chromatogram, after development, is dried and immersed in a large Petri dish containing a 0.2 per cent solution of dithizone in chloroform and subsequently dried again in an oven at a low temperature. A chromatogram showing the separation of the copper group is shown in Figure 3.

SEPARATION OF GROUPS III–V CATIONS

In the preparation of the solutions for use in Groups III–V the nitrates of the metals were used. However, for the separation of the alkali metals the acetates were employed in later experiments because better resolution was obtained with these salts. The concentration of the various salts did not exceed 5 per cent (*W/V*).

TABLE 2

Group IIIA (Aluminum Group)

Type of paper: Whatman No. 1
Time: 1.5–2 hours
Solvent: 40% tertiary butyl alcohol, 40% acetone, 20% 3 *N* hydrochloric acid

Cation	*Identifying reagent*	*Color*	*Rfc*
Al^{3+}	alizarin	red	0.55
Zn^{++}	"	violet	1.00

Group IIIB (Iron Group)

Type of paper: Whatman No. 1
Time: 0.75–1 hour
Solvent: 90% acetone, 10% HCl (6 *N*)

Cation	*Identifying reagent*	*Color*	*Rfc*
Ni^{++}	ammoniacal dimethyl glyoxime	red	0.25
Mn^{++}	"	red-brown	0.35
Co^{++}	"	dark brown	0.65
Fe^{3+}	"	brown	1.00

Group IV (Alkaline Earth Group)

Type of paper: Whatman No. 1
Time: 1.5–2 hours
Solvent: 50% tertiary butyl alcohol, 50% 6 *N* HCl

Cation	*Identifying reagent*	*Color*	*Rfc*
Sr^{++}	potassium rhodizonate	orange	0.35
Ba^{++}	"	red	0.50
Ca^{++}	alizarin	violet	0.60

Group V (Alkali Metals)

Type of paper: Whatman No. 1
Time: 0.75–1 hour
Solvent: methanol (absolute)

Cation	*Identifying reagent*	*Color*	*Rfc*
K^{+}	violuric acid	yellow-brown	0.20
Na^{+}	"	yellow-brown	0.42
Li^{+}	"	violet	0.68

While H_2S was a satisfactory agent for revealing the presence of the cations in Groups I and II, chromogenic agents which gave colored complexes were needed for the other cations.

The identification of aluminum, zinc, and calcium was accomplished by means of a 2 per cent solution of alizarin in alcohol. Barium and strontium were identified with a 2 per cent aqueous solution of potassium rhodizonate. Ammoniacal dimethyl glyoxime was used for identifiying members of the iron group and a 0.2 per cent alcoholic solution of violuric acid revealed the positions of the alkali metals.

Table 2 contains data which were found to separate the cations of Groups III, IV, and V. The Rfc value, chromogenic reagent, and color are listed for each cation. The table also indicates the separations that are possible by developing inorganic mixtures unidirectionally with a single solvent system. Improved separations are obtained by the technique of multiple development, that is, the paper is dried and developed again in the same direction using the same solvent system. This method resolves the zones which originally were diffuse into clear and defined zones.

Circular-paper chromatography places the application of chromatography within the capabilities of beginning chemistry students and also within the budgetary limits of educational institutions. It is a very rapid method of analysis and can be performed within a one-hour laboratory period. The experiments are very simple and can be carried out by even the most inexperienced personnel.

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Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

WATER, A BASIC NATURAL RESOURCE[1]

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NEARLY every course in science at the elementary and secondary levels deals in some way with water. It seems unfortunate with all the emphasis on this vitally important substance that little attention has been given to water as a basic natural resource, indispensable to the development of an industrialized society such as that of the United States. It has been pointed out recently that over 18 tons of raw materials are consumed each year by each person in this country. Much concern is being expressed over the mounting difficulties of securing needed quantities of the various materials comprising these 18 tons. Less attention has been given to the fact that the per capita use of water in the United States averages about 700 tons per year. There are competent students of natural resources who feel the first material to present a critical problem of supply will be water.

With water enough in the oceans to cover the entire earth to a depth of about two miles, it is obvious that this planet is bountifully supplied. However, for the most part, man's needs can only be satisfied by fresh water. Until such time as methods are discovered for economically desalting ocean water and transporting it to places where needed, it is of very limited usefulness. Much research is currently in progress, looking toward the production of fresh water from ocean water. At the present time it seems likely that energy will be the critical factor in utilizing ocean water. For example, to produce the fresh water consumed in the United States in 1950 from sea water would have required the energy equivalent to two billion tons of coal, which is a little more than the total energy used in the United States during that year. For the present, then, fresh water naturally available on the earth constitutes the resource upon which man can draw.

Fresh water, unlike most other mineral resources, is renewable. It is a part of a gigantic circulatory system powered by solar radiation in which water evaporates into the atmosphere, is transported, and precipitates in an endless cycle. The maximum water resource of a region is the amount of precipitation. Man uses water simply by creating a detour in the water cycle.

The water precipitated on the United States amounts to about 4300 billion gallons per day on the average. For very few other resources is the available supply known so exactly. This astronomical average quantity of water available daily tends to produce an unwarranted sense of security. Actually, about 3000 billion gallons of this water are lost to man's use daily, on the average, through evaporation and transpiration by plants.

Thus, a maximum of about 1300 billion gallons are available daily for municipal, industrial, and other uses. The water which is transpired by desirable trees and by food, fiber, and other useful crops is beneficial to man but, nevertheless, is not directly available for use in the ordinary sense. It is obvious that transpiration occurring in plants of no value to man represents waste. In some arid areas of this country steps are already being taken to conserve water by destroying mesquite and other useless vegetation. It has been calculated that the water resources of the state of Arizona could be increased by as much as 600 million gallons per day by the elimination of all useless vegetation. It is conceivable that at some time in the future water will be in such short supply that it will be essential to limit the growth of vegetation to those plants directly useful to man. It is clear that such action involves tampering with the biological balance of nature to an extent almost inconceivable and with consequences that can be determined only by an enormous amount of research.

The average 1300 billion gallons of water currently available for man's use daily in the United States is called runoff. A part flows rather rapidly over the surface of the land into streams and rivers and hence to the oceans. Another portion percolates into the soil and the cracks of rocks to become ground water. It must be emphasized that ground water ultimately reaches the oceans, too, but its rate of motion is much

[1] Presented at the 16th Summer Conference of the New England Association of Chemistry Teachers at the University of Massachusetts, Amherst, Massachusetts, August, 1954.

slower than the surface water of rivers. It may take ground water years or even centuries to traverse the narrow interstices in rocks and soil to the oceans.

There is a very large quantity of water in storage in the United States. It is estimated that there are about 6000 cubic miles of water stored in the natural and artificial reservoirs of this country. About 5000 cubic miles of this stored water is in the Great Lakes. It is believed that the amount of ground water is considerably greater than that stored in surface reservoirs. Even though ground water is constantly on the move toward the oceans, its rate is so slow that it can properly be considered as water in storage. The total water in storage represents 20 or more years of average runoff. For some reason, many people fail to distinguish between stored water and precipitation, particularly with respect to ground water. It should be quite obvious that stored water is nothing more than the precipitation of earlier years. If stored water, whether surface or ground, is used at a rate in excess of replenishment, it must eventually be used up. Stored water is extremely useful to man. It provides a source of supply during periods when precipitation is less than normal. It may have properties which make it more desirable than surface water. For instance, much ground water is used in air conditioning because it has a lower and more uniform temperature than surface water. In the long run, however, the safe maximum quantity of water that can be used is fixed by the amount of runoff.

During the last few years much publicity has been given to the drop in the water table which is the surface below which the interstices in soil and rocks are completely filled with water. This publicity has been so effective that a great many persons have become convinced that the water table has become drastically lowered over the entire country. This is by no means true. In certain areas, as in portions of the dry plains, and in parts of the Central Valley of California, water has been pumped from the underground reservoir at a rate far in excess of normal replenishment. In these areas, the water table has fallen so seriously that real problems have been created. Over most of the country water tables have been lowered seriously only in small, localized areas. It is well to point out that there would be no problem of lowered water tables if man had not been so successful in devising efficient pumps and providing low-cost power to operate them.

Far too little is known at present about the underground reservoir beneath large areas of the country. Before it can be determined what quantity of water can be safely removed from the ground, much more needs to be known about the capacity of the reservoir, the rate at which water travels through it, and the areas through which precipitation enters the ground to recharge it. When such facts are known the reservoir may be operated as efficiently as the artificial reservoirs of a municipal water supply system.

Average figures for an area as great as the United States do not give a true picture of the water supply available in most local areas. For example, the total precipitation is equivalent to 30 inches per year for the entire country. Actual precipitation varies from as little as an average of 2 inches per year in Death Valley to as much as 160 inches at certain points in the Puget Sound area of the Pacific Northwest. Except for relatively small areas along the Pacific Ocean, the average precipitation in the great area of the 17 western states is from 5 to 20 inches per year. The eastern portion of the country receives from 30 to 60 or more inches of precipitation.

Even the average figures for a given locality are misleading, for the precipitation may vary considerably from year to year. Furthermore, the precipitation may not be evenly distributed throughout the year. Boston, Massachusetts, is an example of a locality in which precipitation on the average is rather evenly distributed. Monthly average precipitation for this city ranges from 3.1 inches to 3.7 inches. For Grand Junction, Colorado, the range is from 0.6 inch to 1.1 inches per month on the average. The distribution is relatively even, but the total quantity is small. On the other hand, in Los Angeles, California, the average precipitation for July and August is virtually zero, but in January and February it is over 3 inches per month. Again, it must be pointed out that monthly averages do not give a very true picture of available water supply. For example, in certain years there may be many weeks in which rainfall is much below the average. On the other hand, a single storm lasting only a few hours may bring precipitation exceeding the average for the whole month.

Over considerable areas of the country there is another factor which creates irregularities in the quantity of water available. In those sections where average temperature drops below freezing for a part of the year, precipitation occurs as snow. Such precipitation does not become runoff until some later time. In such regions, additions to immediately useful water supply through precipitation may be entirely absent for months at a time.

The wide variations in distribution of precipitation both in time and place is the crux of most of the currently pressing water-supply problems of the present. If all parts of the country were to receive 30 inches of rainfall per year in gentle showers occurring two or three times a week, our water-supply problems would be much different. Efforts to induce precipitation artificially by cloud seeding or similar processes are aimed at regulating the time and place of precipitation. The present state of research in this field does not allow confident prediction that widespread control of the process of precipitation is likely in the immediate future, although one cannot be certain that this will always be the case.

In connection with artificially induced precipitation, the question arises as to whether it may be possible to increase the total precipitation as well as to regulate the time and place at which it occurs. There are some scientists who feel that a more complete understanding of the whole intricate phenomenon of the water cycle may make this possible. Environmental control on a

scale envisioned by such scientists seems rather remote at the present time.

An understanding of the wide variations in precipitation serves to emphasize the tremendous importance of stored water. If agricultural uses of water are excluded, man's need for water tends to be fairly uniform day after day. Of course, there are relatively minor fluctuations in demand for water which are related to the seasons and to industrial activity. The storage of water in times of plentiful rainfall is the only feasible way, at present, of insuring regularity of supplies. This fact has been recognized from early times. The rain barrel by the colonial farmhouse, the cistern, and the artificial reservoir are evidences that man recognizes the desirability of storing water.

The adequacy of our water supply of 1300 billion gallons per day can be ascertained by considering the demands that are placed on it. The primary demand, of course, is for drinking water. The average consumption of water by a human being is about 200 gallons per year or a little more than a half-gallon per day. Thus, somewhat less than 100,000,000 gallons of water per day are sufficient to satisfy the biological needs for water of the entire population of the country.

One of the prices that man has to pay for civilization is a need for water far beyond that for drinking purposes. The development of habits of cleanliness, the cooking of food, and the construction of heated and, more recently, air-conditioned homes, has created demands for water which amount on the average to about 15,000 gallons per year or 40 gallons per day, per person in the United States. This quantity is dwarfed by the water used by the industries of the United States which amounts to an average of 160,000 gallons per year, or over 400 gallons per day, per person. For example, five gallons of water are required to process one gallon of milk; ten gallons or more to produce a gallon of gasoline; 80 gallons for the generation of one kilowatt-hour of electricity; 300 gallons to manufacture one pound of synthetic rubber, and 65,000 gallons to make a ton of steel. The largest single use of water in the United States is for irrigation. In 1950 there were about 26,000,000 acres of land being irrigated, which required an average of 88 billion gallons of water per day. That represents an average of over 500 gallons per person per day. The quantity of water needed to mature a crop is tremendous. It has been calculated that to grow one cutting of alfalfa requires about 325,000 gallons of water per acre. About 800,000 gallons of water per acre are needed to produce one crop of cotton. This raises the question as to whether irrigation in water-short areas represents the best use of available supplies.

All these uses for water required, in 1950, the enormous total of 170 billion gallons per day or about 13 per cent of the average annual runoff. In addition, about 15 billion gallons of brackish or salt water are used daily for certain purposes by industries located near the oceans. It is important to emphasize that the use of water often does not mean that it is consumed. In a strict sense, water is not consumed unless it becomes chemically united with something else or is evaporated. For example, most of the water used in the generation of electricity serves as a cooling agent only. That water is usually returned to the river or other body from which is was obtained, unchanged except in temperature. Such water can be, and often is, reused. On the other hand a large part of the water used for irrigation is evaporated or transpired and is thus truly consumed since it is no longer subject to reuse. The figure 170 billion gallons represents the total amount of water withdrawn from natural sources. It includes considerable water which has already been used. No reliable figures are available concerning the amount of reuse. Thus, it is seen that at present the United States is probably consuming less than ten per cent of the maximum available supply of water.

This may seem a comfortable situation until the probable demand for water in future years is considered. The United States is at present growing rapidly in population. It seems quite likely that by 1975 the population will exceed 200 million, an increase of over 30 per cent above the population of 1950. At the same time industry is expanding at an even more rapid rate. Additional lands—as much as six million acres—will be brought under irrigation. The rapid growth of supplemental irrigation in many areas, for example in New England, will add to the demand for water. Considering all likely demands for water, it seems probable that the withdrawal of water in the United States in 1975 will be about double what it was in 1950, or perhaps 350 billion gallons per day. Since a part of this withdrawal will be reused, it would seem that there is still a comfortable margin between water used and the maximum amount available. If, however, we note that it has taken this country some 300 years to develop the need for 170 billion gallons per day in 1950, and that the amount seems likely to double in the next 25 years, it becomes apparent that rapidly accelerating demand for water may overtake available supply much sooner than one cares to contemplate.

So far in this discussion little mention has been made of the changes in water supply that man has brought about by his occupancy of the land area of the United States. When the first white people arrived in this country they found the land supporting a cover of trees, grass, or other vegetation. The cover of vegetation had an effect in regulating runoff. That water which ran over the surface was impeded by vegetable litter covering the ground so that it reached streams and rivers more slowly. At the same time, the slow movement of water over the ground allowed ample time for percolation to the ground-water reservoir to take place. While it is certain that unusual weather and climatic conditions at times produced rapid surface runoff and consequent flooding of rivers, it is equally certain that the flow of precipitation to the oceans was a relatively orderly and uniform process.

During the last 300 years very significant changes have been made in the surface of the land. Vast

acreages of forests have been cleared, grasslands have been converted into farmlands, dry and desert areas have become grazing lands, thus materially changing the extent and character of the cover of vegetation. There is rather clear evidence that the physical structure of some soils has become changed by agricultural use so that it is much less permeable to water. In addition, several millions of acres of land have been waterproofed by covering them with buildings, and with asphalt and concrete-surfaced roads and airports. Often carefully engineered drains are provided to hasten the runoff from such structures. The result of these changes has been to increase the rate and quantity of surface runoff, as evidenced by frequent and violent flooding. It is customary to think of floods in terms of loss of life, human misery, and destruction of property. These are matters of grave concern without question; but in terms of water resources, floods represent an enormous waste. Such water cannot be put to use and represents a very significant reduction in the total amount of water available.

The control of floods is a major problem in the utilization of water resources. Vast sums of money have already been spent for protective works around cities and for reservoirs to impound flood water. There is a growing realization that the way in which the land of a watershed is used and managed has an important bearing on floods and their control. Thus farms, pastures, and woodlots may be contributory causes to destructive flooding that occurs hundreds of miles away.

While it is clearly recognized that the control of flood waters is a problem which must be solved, there is a vast amount of controversy as to the best methods to be used, the source from which necessary funds should be drawn, and the authority which should administer them. At the present time, there is a confusing array of federal, state, and local governmental agencies as well as private agencies involved in flood control activities with resulting conflicts of interests and authority.

During the last 300 years another important change has taken place in the water resources of the United States. From the earliest days of the country, flowing water has been used for the disposal of waste materials. Within certain limits this is a feasible and proper use of rivers, for the biological and chemical phenomena which take place in natural waters are capable of converting many types of waste materials to harmless and nonobjectionable substances. With the growth of urban population, an ever larger quantity of sanitary wastes was added to rivers. At the same time industrial wastes in rapidly increasing volume and variety were being contributed. As a result, most of the major rivers of the nation as well as hundreds of smaller rivers and streams are today loaded with wastes far beyond the natural capacity of the water to render them innocuous. The enormous quantity of wastes added to rivers in this country is not generally realized. For instance, it is estimated that the Delaware River receives 500 million gallons of domestic sewage and as much or more industrial waste each day. In times of low flow the Ohio River at Cincinnati is at least one-half made up of water already used for waste disposal. Even rivers in primarily agricultural regions may be charged with silt or with dissolved salts as a result of repeated use of the water for irrigation.

The effects of pollution of waterways are manifold. Aesthetic and recreational values are destroyed, as well as sport and commercial fishing. Furthermore, pollution seriously limits the use to which water can be put. When a river becomes grossly polluted in its upper reaches, the water may be entirely unfit for use farther down stream without expensive purification. Thus, pollution tends to reduce the total quantity of water available almost as effectively as do floods.

The problem of eliminating pollution in this country is an enormous one. It involves some 20,000 major sources of pollution, about equally divided between municipalities and industrial plants. Furthermore, many rivers cross state boundaries, making necessary cooperative action between states and possibly the federal government for effective action. The cost of pollution control will be very large. Since 1915 some ten billion dollars has been expended on plants for the treatment of municipal sewage. At least as much more needs to be expended for treatment plants for municipal sewage. A like amount is needed for the treatment of industrial wastes. It is a heartening fact that there is widespread concern over pollution of water and that real, though slow, progress is being made to eliminate it. Industry, in particular, is becoming increasingly aware that it is a matter of good public relations to avoid pollution of rivers.

The net result of accelerated runoff and pollution is to reduce the supply of water of directly usable quality to a point much closer to current demands than the total average runoff would indicate. It is estimated that none of the states which use the largest quantity of water, with one possible exception, could double the available supply without very large costs. Already many industries which need large quantities of water are finding considerable difficulty in locating sites which provide water of suitable quality.

There are many other problems involved in the utilization of water resources of this country, which are beyond the scope of this paper. How shall water in arid areas be allocated between agriculture and industry? Should water be used to provide navigation on inland waterways? What shall be the place of hydroelectric developments in the total water usage scheme? To what extent is it the responsibility of the federal government to develop and administer a broad program for efficient control and use of water resources? In whom should rest the responsibility for needed scientific research related to water resources? If this country is to be supplied with adequate quantities of water, the solution to all these problems must be found in some sort of a broad plan which recognizes the multiple demands for water and provides an integrated program for satisfying them.

To the Editor:

The readily apparent inequities in the scoring method presented by Scott MacKenzie in "Proper place problems," THIS JOURNAL, **31**, 428–9 (1954), lead me to offer a method I have found both indicative of the student's grasp of the subject and simple to use.

The statistical method presented by Mr. MacKenzie ignores relative positioning of answers, and neglects near misses. In a series correctly placed 1, 2, 3, 4, should a student answer 4, 1, 2, 3, he would receive no credit at all by this method, for all four answers are out of their places. Surely the fact that the student put 1, 2, 3 in correct relative order shows some knowledge. A student who, asked to list the states in the order that they entered the United States, lists Arizona first, but follows this with the rest from Delaware through New Mexico in proper order, surely shows knowledge far greater than chance. Yet this method would give him no credit, because all of the states would be listed out of their proper places! In the first example cited by Mr. MacKenzie, a student has placed the weakest and strongest acids in their proper positions, but inverted the intermediate two. It would have been far worse if the student had misplaced the extremes in the group, since less comprehension of the properties of the compounds, the theory of acidity, or other essential knowledge would have been indicated. That is, 4, 2, 3, 1 is worse than 1, 3, 2, 4, although both receive the same credit by Mr. MacKenzie's method. In the second example, a student has shown flagrant ignorance in listing 1-butene as the highest boiling compound, but would be penalized the same amount for the much less serious error of listing *n*-butane as the lowest boiling compound. It is well to consider the amount of displacement and relative positioning in errors in proper place problems, as well as the mere fact that error has been committed. This can be achieved simply by the following method.

TABLE 1
Scoring of Answers to Four-part Proper Place Problem

Item	*Correct*	*Example 1*	*Example 2*	*Example 3*
1	HF 4	HF 4	CH_4 −2	H_2O 2
2	H_2O 4	NH_3 2	NH_3 2	NH_3 2
3	NH_3 4	H_2O 2	H_2O 2	CH_4 2
4	CH_4 4	CH_4 4	HF −2	HF −2
Series	0	0	0	3
Total	16	12	0	7
Per cent	100	75	0	44

Each item in the answer is allotted a point value equal to the number of items (four in Mr. MacKenzie's first example, six in his second, 48 in the example of the states). Two points are removed from this value for each unit or position the student's item is displaced from its proper position:

No. items in list	4				6					
No. positions displaced	0	1	2	3	0	1	2	3	4	5
Score for item	4	2	0	−2	6	4	2	0	−2	−4

To give credit for relative placement of some items, one point is added to the total score for each item in a series longer than two items placed in correct relative positions, but not in correct absolute positions. The scores can then be placed on a per cent basis, and the computed per cent of any nominal score for the question taken. Examples based on Mr. MacKenzie's first list are given in Table 1, those based on the second list in Table 2. In each table, Example 1 is the order cited by him. Example 2 is the worst possible answer, reversal of order.

It may be admitted that this method does not adequately recognize the greater difficulty of longer lists, but the experienced teacher is likely to reserve long series for more mature students. These should be as capable of solving them as neophytes are the shorter ones. This is no worse than expecting advanced mathematics students to solve problems involving calculus, but requiring only simple arithmetic of grade-school pupils.

TABLE 2
Scoring of Answers to Six-part Proper Place Problem

Item	*Correct*		*Example 1*		*Example 2*		*Example 3*		*Example 4*	
1	Acetic acid	6	1-Butene	−4	1-Butene	−4	Acetic acid	6	Acetic acid	6
2	1-Propanol	6	1-Propanol	6	Butane	0	Acetone	4	Acetone	4
3	Acetone	6	Acetic acid	2	Methyl formate	4	Methyl formate	4	Methyl formate	4
4	Methyl formate	6	Methyl formate	6	Acetone	4	1-Butene	2	Butane	4
5	Butane	6	Acetone	2	1-Propanol	0	Butane	6	1-Butene	4
6	1-Butene	6	Butane	4	Acetic acid	−4	1-Propanol	−2	1-Propanol	−2
Series		0		0		0		0		4
Total		36		16		0		20		24
Per cent		100		44		0		56		67

It may also be admitted that this method carries no guarantee of absolute justice; for example, the worst possible arrangement of proper place items is reverse order, yet, where consistent, this surely means knowledge of some sort, perhaps perfect knowledge of the material, but incorrect reading of the problem. Student answers at best involve a degree of uncertainty of motives, conditions, and personal errors that only omniscience or mind reading could fathom. The teacher's good judgment is required in every individual evaluation. Statistics and other mathematical systems are no substitute for this. I believe, however, that this method is more help to judgment than the statistical method presented by Mr. MacKenzie. Perhaps a combination or compromise between these methods could be effected. I should be interested to see what might be evolved.

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To the Editor:

The communication of Mr. L. O. Smith expressed certain criticisms of a method of grading proper place problems which was recently proposed. I desire to answer these criticisms and to deny that the alternate proposal is as good or better. In what follows, the original proposal will be referred to as method *A*, while the alternate will be method *B*.

Smith states that method *A* "ignores relative positioning of answers and neglects near misses." Quite true; but this fact should not be considered as a *fault* of method *A* but one of its main assets. For if a student does not know one pair of items in a list of four, he might write 4, 2, 3, 1 or 1, 3, 2, 4 or some such combination. Why should lack of knowledge of one pair be worse than lack of knowledge of another just because one pair happens to involve the end items?

That property of method *A* which is most frequently criticized is also discussed by Smith. It is illustrated by the sequence 6, 1, 2, 3, 4, 5. He points out correctly that by method *A* the student would receive 0. This argument appears damning at first sight, but it is, I feel, artificial and highly contrived. It makes two assumptions: first that the student knows well 1, 2, 3, 4, 5 but is *totally* ignorant of 6; this might be true but is usually not in questions in chemistry; I have never encountered such a mistake in grading lists longer than four items. Second, it assumes that the student, bright enough to know 1, 2, 3, 4, 5 and totally ignorant of 6, then has not enough sense to place the unknown in the middle of the list so that, by *any* system of grading, he suffers less! A third point should be made in refutation: Students generally remember best the highs and lows (the strongest acid, the most densely populated state, the longest rocket flight, etc.), and this is probably the chief reason that arrangements such as 6, 1, 2, 3, 4, 5 are almost never seen. I feel that there is no particular merit in this, but it is true and emphasizes that this criticism of method *A* is largely manufactured.

It is interesting to consider method *B* as a possible alternate method. For several answers it does *appear* more equitable, but my objections to this method are twofold. First, it is much more generous (and thus appears more equitable). By method *B* a student has an expectancy over double that by method *A*.

Items	*Expectancy, method A*	*Expectancy, method B*
3	17%	47%
4	16%	35%
5	16%	37%
6	16%	...[1]

Thus, in comparing the two systems, one must not confuse generosity with equity.

A second objection to method *B* is, I feel, much more fundamental. It assumes that the grader knows with absolute certainty, on seeing any answer, the knowledge held by the student. Thus in the sequence 5, 2, 1, 3, 4 the grader says, in effect, "The student knows 2, has a good notion of 3 and 4, is poor on 1 and badly off on 5; he deserves 28 per cent." This is sheer guesswork. By method *A* the grader always asks, in effect, "Has the student written an answer which, *on the basis of probability*, enables me to feel that he knows something of the question?" One must say "no" in reference to the above sequence.

I shall continue to consider with interest alternate methods. Method *A* may ultimately give way to a more advantageous system. I do not feel that method *B* is that system.

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[1] Those wishing to apply method *B* to higher lists can calculate the expectancies. The set indicated has 720 answers to be graded, added, and averaged.

To the Editor:

Proper order problems of the type, "Arrange in decreasing order: $^3/_5$, $^5/_3$, 0.1, $^1/_4$, $^1/_2$" are often posed in chemistry to test the knowledge of the relative orders of some property such as melting point, acidity, activity, etc. Grading is simple as long as full credit is given only for the perfect answer and any mistake reduces credit to zero. However, if it is desired to assign partial credit to incorrect answers, the rational procedure may not be obvious. MacKenzie (THIS JOURNAL, **31**, 428 (1954)) has proposed a procedure which has been criticized by Smith, who offers a substitute approach. I would like to present an analysis of the basic premises involved and some consequences with respect to grading and the meaning of this type of problem.

Let us first distinguish between proper *order* and proper *place* problems. The former asks for the relative positions of items, as in the above sample; the latter asks for the position of each item in a series, for ex-

ample, "Place according to their position in the second period: Be, B, N, Ne, F, Li ,C, O," or simply, "Which element has atomic number 8?" Both types have their merits. The former tests the appreciation of relative values of scattered items, the latter their position in a significant absolute series. On the other hand, I can see little point in testing the knowledge of position in an unimportant and arbitrary or *ad hoc* series. Thus, if the first problem were rephrased to, "Which is the fourth when the following fractions are arranged in decreasing order?" it would not seem to me to test any knowledge more important than that of their relative magnitudes.

The series 1, 2, 3, 4 discussed by Smith is an important one and I would use it as the basis for a proper *place* problem.

While the relative merits of the two types of problem may be subject to argument, it is certainly important not to grade inadvertently a proper *order* problem as a proper *place* one. This is precisely what happens, however, if the grading is based on a comparison of the answer with the correct series and marking as right all the coincidences. Such procedure is certainly the easiest and seems to be the one suggested by MacKenzie. Consider the student who, in our simple example, understands all the relative values except that of the smallest fraction and places it first:

$$0.1,\ {}^{5}/_{3},\ {}^{3}/_{5},\ {}^{1}/_{2},\ {}^{1}/_{4} \qquad (1)$$

None of the items coincides with the correct series and as a proper *place* problem the answer is indeed worthless. As a proper *order* problem, however, it certainly deserves some partial credit. On the other hand, the answer:

$$0.1,\ {}^{3}/_{5},\ {}^{5}/_{3},\ {}^{1}/_{4},\ {}^{1}/_{2} \qquad (2)$$

seems to me to show little discernible appreciation of relative magnitude, yet two items correspond to the perfect series and a credit of 55 per cent is assigned by MacKenzie's method.

The method suggested by Smith takes into account mainly the displacement from the true position which corresponds to the number of relations missed. This measure breaks down, however, when the displacements cross. This correspondence is ambiguous as may be seen from the fact that 2, 1, 4, 3, and 1, 4, 3, 2 both involve displacement by four places but the former misses two relations (1–2, 3–4) while the latter misses three (2–3, 2–4, 3–4).

If the premise that proper order problems should test the knowledge of relative positions is accepted, it would seem that grading should be based on the number of pairs which are in the correct relation. Such counting takes a few moments, but by proceeding methodically we find that in the perfect series of our five fractions, the first is correct with respect to four succeeding items, the second with respect to three succeeding ones, etc., so that there are altogether ten correct relations. Of these ten, answer (1) shows six and answer (2) shows only four, in agreement with our qualitative estimate of the two.

Will we now wish to give 60 per cent and 40 per cent credit, respectively, for these two answers? If we do, the students will be quite happy and the class average high. At first sight it may seem that the fraction of correct relations to be obtained by chance decreases as the series gets longer and should be small for a series of five items. In fact, however, this fraction is independent of the length of the series and always equal to 0.5. This is simply due to the fact that any one item can find itself only either ahead or behind a given other item within the series and the chance of either happening is equal. So the chance of any one relation being correct is 0.5, so that on the average 0.5 of all relations will be correct.[1] Hence the assignment of 20 per cent credit to (1) and 20 per cent debit (if there is any chance of collecting) to (2) would seem more rational and would agree with my subjective evaluation.

It follows from the above that when it comes to proper *order* problems, a series of *two* does not involve any more of a chance element than a long one. The series of two has the great advantage over any other that it has only one correct and one completely incorrect answer, so that all partial-credit problems are completely eliminated and grading is greatly simplified. In fact, a series of two can be best put into the familiar true-false form. Thus any information about the student's knowledge which is given by a proper *order* problem is exactly equivalent to the information from a corresponding series of true-false questions.

The transformation of a proper order problem into a series of true-false questions requires more space since n items are replaced by $n(n-1)/2$ questions. A brief consideration will generally reveal, however, that many of these questions are trivial (or too difficult) and can be eliminated, so that this should not be an important objection.

To summarize: The proper *place* problem is useful in the pedagogical arsenal and its partial credit assignment may well be conducted according to MacKenzie's analysis. The proper *order* problem is, however, of a completely different type and should be graded differently. If no partial credit is to be given, its difficulty increases and the chance element decreases rapidly as the series is lengthened. If partial credit is to be given, however, it can be replaced to advantage by a series of true-false questions.

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[1] The following more formal proof may seem more convincing to some. If n is the number of items, then of course (a) the number of correct relations in the correct answer is $n(n-1)/2$; (b) the number of possible different answers is $n!$ The number of correct relations X_n among all these answers can be expressed as a function of X_{n-1}. If the n'th item which should be in the n'th position is added to any series of $n-1$ items, it will add no correct relations if placed first, one if placed second, etc., for a total of $n(n-1)/2$ added relations in n answers, and since there are $(n-1)!$ such series, $X_n = nX_{n-1} + n(n-1)(n-1)!$ Since $X_1 = 0$ it is easily verified that $X_n = n!n(n-1)/4$ which is exactly half of (a) times (b).

To the Editor:

In a recent article MacKenzie discusses the grading of "proper place problems," such as "arrange in order of decreasing acidity water, ammonia, hydrogen fluoride, and methane." Questions of this type are an excellent test of the student's knowledge and reasoning powers, but proper evaluation of the answers certainly presents the instructor with problems of his own. MacKenzie concludes that the student's grade should be calculated by a combinatory formula based upon the number of items listed in the correct place. The use of *place* as a criterion seems questionable when both the intention of the question and its actual wording call for the use of *order* relationships as a basis for the answer. This could more aptly be called a "proper order problem."

Since the student is expected to use order relationships to formulate his answer, a fairer method of grading such questions might be one based upon the number of correct orderings which the answer shows. The grade could be taken as the ratio of the number of correct pairings in the answer to the maximum possible number. (The latter is $n(n-1)/2$ when there are n items to arrange). Trying to read the student's mind is often an unprofitable task, but the instructor must make a stab at it when *partial* credit is to be given for an answer. The order criterion seems to give such credit more equitably than that of place. Consider the cases below.

(1) To the acidity question above the answer H_2O, NH_3, CH_4, HF is given. By the place test the student gets zero since all items are misplaced. Actually, the student knows that H_2O is less basic than CH_4 or NH_3 and that NH_3 is more acidic than CH_4, but he is badly misinformed about HF. Since he has three of the six pairs ordered rightly, his grade could be 50 per cent.

(2) To the same question the answer H_2O, NH_3, CH_4 is given. No grade at all is possible by the place test, since the instructor cannot tell whether these were meant to be in first, second, and third or second, third and fourth places. By the order test this student knows just what student (1) did and gets the same grade.

(3) To the question of arranging the following gases in order of increasing density under standard conditions, these two answers are received: H_2, HCl, NH_3, CH_4, BH_3, and He; H_2, He, CH_4, NH_3, HCl, and BH_3. Each answer has two items correctly placed and is graded 49 per cent by the place formula. However, the first student actually knows that hydrogen is the lightest gas but not much else, whereas the second understands the problem but does not know the atomic weight of boron. The first answer has five of the 24 pairs ordered rightly (21 per cent) while the second has 21 in the right order (88 per cent).

When all possible answers are recorded and the numbers of correct pairs plotted against the frequency with which they occur, a symmetrical curve is obtained with its maximum at half the total number of pairs. Random guessing would thus give half this total as the most probable result. To reduce guessing, the grade may be based on the difference between the numbers of pairs right and pairs wrong, in analogy to the way a set of true-false questions is often graded. Students should be informed in advance if this system is to be used.

With a large number of items, pair-counting becomes very laborious. I recommend that any teacher employing this order or "mind-reading" criterion limit the number of items to be arranged to from six to seven.

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To the Editor:

The recent publication (KIRBY, H. W., *Anal. Chem.* **26,** 1063–71 (1954)) of decay and growth tables for the naturally-occurring radioactive series prompts the remark that there is a little known but useful graphical method for similar purposes. The method has been regularly rediscovered—if indeed, discovery is the correct term to apply—but despite its value has not to my knowledge been published. The method is implied in Friedlander and Kennedy's "Introduction to Radiochemistry" (John Wiley & Sons, Inc., New York, **1949**) on pages 109 to 116 and in Figures V-2 on page 11 and Figure V-3 on page 113, but the simplicity and power of the method are not discussed; nor are any details of the method to be found in Friedlander and Kennedy.

The method will be described in connection with the Bateman equation for the activity of a second decay product relative to the initial activity of a parent which was pure at $t = 0$. The equation for this case is given by Kirby—his equation (3)—as:

$$\frac{N_3\lambda_2}{N_0\lambda_1} = \lambda_2\lambda_3\left[\frac{e^{-\lambda_1 t}}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)} + \frac{e^{-\lambda_2 t}}{(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)} + \frac{e^{-\lambda_3 t}}{(\lambda_3-\lambda_1)(\lambda_3-\lambda_2)}\right]$$

when all symbols have the same significance assigned by Kirby.

First compute the three quantities:

$$\frac{\lambda_2\lambda_3}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)}, \quad \frac{\lambda_2\lambda_3}{(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)}, \quad \frac{\lambda_2\lambda_3}{(\lambda_3-\lambda_1)(\lambda_3-\lambda_2)}$$

The term $\lambda_2\lambda_3$ is, of course, common to all three and need only be computed once. Except for sign, there are only three other terms which appear and these are $(\lambda_1 - \lambda_2)$, $(\lambda_2 - \lambda_3)$, and $(\lambda_3 - \lambda_1)$. Accordingly, these need but one computation. Now for convenience call the left side of the Bateman equation y and rewrite the right side as

$$M_1e^{-\lambda_1 t} + M_2e^{-\lambda_2 t} + M_3e^{-\lambda_3 t}$$

At this point the M's have been computed. Treating the M's as positive, plot the points $(0, M_1)$, $(0, M_2)$, and $(0, M_3)$ on semilogarithmic paper. Y is, of course, plotted on the logarithmic scale and t on the linear one.

Now, plot the points $\left(T_1, \frac{M_1}{2}\right)$, $\left(T_2, \frac{M_2}{2}\right)$, $\left(T_3, \frac{M_3}{2}\right)$.

Generally the value of T_n will be available when λ_n is,

but if not, it is readily computed. Using a straight edge construct the three lines determined by the pairs of points $(0, M_1)\left(T_1, \frac{M_1}{2}\right)$, $(0, M_2)\left(T_2, \frac{M_1}{2}\right)$, and $(0, M_3)\left(T_3, \frac{M_3}{2}\right)$.

The final step is to add, with due regard to sign, the values read from the three straight lines at suitable time intervals, plot the sums on the same sheet, and then draw the curve of y as a function of t.

It is convenient to have a scissors and Scotch tape handy to extend the graph paper when it appears that longer times and a few more decades of the y axis are needed. A check on the computation may be made by observing that $M_1 + M_2 + M_3$ must equal zero, for at $t = 0$ the negative exponentials are all unity, and the activity of a second decay product must at $t = 0$ also be zero.

The accuracy of the graphical constructions may be increased by the use of larger graph paper, but even a small plot gives a wealth of useful information. For example, the graphically produced plot may be used to estimate in which regions to make more accurate numerical computations or serve as a rough check on the results of more accurate computations. The work needed for Bateman equations with more terms does not become prohibitive. A similar technique is, of course, applicable to the decay curves of mixtures of radioactive substances in which no parent-daughter relationship exists. The method is short enough to be recommended for assignments to students.

Kirby's warning that the Bateman equations deal only with such quantities as numbers of atoms, decay constants, etc., and not with the nature and energy of the radiation, self-absorption of samples, counter sensitivity, and geometry is worth repeating. The latter are always to be reckoned with and may be taken into account after applying the Bateman equation.

GEORGE L. BUC

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To the Editor:

The article by Dr. Holmes dealing with "The growth of colloid chemistry in the United States" (THIS JOURNAL, **31**, 600 (1954)) carries the names of many individuals prominent in the development of colloid chemistry. One name that is absent, however, is that of Edward Goodrich Acheson, whose deflocculation of clays antedates W. R. Whitney's work on colloidal gold by one year.

In 1901 Dr. Acheson demonstrated the manner in which organic matter may be utilized to deflocculate (or colloidalize) clays. (See ACHESON, E. G., "Deflocculation," *J. Ind. Eng. Chem.*, **4** (1912).)

Applying these same techniques to graphite, Acheson in 1906 rendered graphite colloidal. (See ACHESON, E. G., "Deflocculated graphite," *J. Franklin Inst.*, **164** (1907).)

While Dr. Acheson is best known for his achievements in electrochemistry, as the inventor of the electric furnace bearing his name, and as the first to prepare silicon carbide and synthetic graphite by electrothermal means—later making these vitally important articles of commerce—his pioneering work in applied colloid chemistry should not be overlooked.

RAYMOND SZYMANOWITZ

ACHESON INDUSTRIES, INC.
NEW YORK, N. Y.

● YEAST TECHNOLOGY

John White. John Wiley & Sons, Inc., New York, 1954. xvi + 432 pp. 71 figs. 59 tables. 14.5 × 22.5 cm. $8.

A SYNTHESIS of "the important biological factors governing yeast growth and development, together with an account of modern methods used in the industrial propagation of yeasts" is the substantial task which the author has set for himself in "Yeast Technology." Mr. White has attempted to achieve this end by the use of data gleaned from his considerable experience with the growth and commercial production of baker's yeast as a basis for extrapolation to the problems of yeast culture in general.

That the latter part of the author's prospectus has been broadly and thoroughly covered is made manifest by the names of some of the chapter headings dealing with the industrial production of yeast. These include Baker's Yeast; Modern Practice in Production of Baker's Yeast; Control of the Assimilation and Harvesting of the Yeast Crop; The Importance of Nutrilites in the Production of Pressed Yeast; Microbiological Control of Yeast Growth Processes; Yeast Products; Dried Baking Yeast; Some Aspects of the Behavior of Baker's Yeast in Panary Fermentations; and several others. These chapters detail much original work and bring together many hitherto scattered references. The close attention to detail is shown by the chapters

dealing with the statistics of yeast growth wherein attention is paid to the calculation of the growth coefficient and its considerable relevance to fermentation practice.

However, the "important biological factors governing yeast growth" fare less well in this book. Even admitting that a synthesis of the voluminous literature on yeast growth would be impossible, many glaring omissions are at once apparent. The enzymes of fermentation and oxidation are relegated to a small and not very inclusive table entitled "Some of the more important yeast enzymes." Furthermore, the author speaks of an "entirely unknown battery of enzymes" as being involved in the aerobic growth of yeast, even though this phase of yeast biochemistry has progressed to a point where many fruitful possibilities are open to the fermentation chemist. Mention need only be made of Horecker's recent review in *Brewer's Digest* (**28**, 214–19 (1953)) as evidence for the large fund of knowledge that has been accumulated on "shunt" or pentose metabolism.

A specific instance wherein the author has failed in his original intent is demonstrated by his handling of the interesting data he presents in Figure 69. This work shows very clearly that maltose when mixed with dextrose is not fermented until all of the dextrose is utilized. Monod's classic work on exactly this phenomenon in bacteria, which he termed diauxie, is not even mentioned, even though these are the most detailed data in the field. Moreover, the induced synthesis of enzymes (adaptive enzymes), upon which the fermentation of several sugars (including maltose) depends is not even mentioned by name but is described as a generalized adaptation phenomenon (pages 386–7). Finally, it should be mentioned that the important work of Ephrussi and co-workers on cytoplasmic mutations has been omitted from the chapter on genetics.

Apart from errors of omission are the dangers in extrapolating from one strain of yeasts to others. Thus the author lists uranium as a nontoxic mineral in his experiments, whereas other work (Rothstein, Guzman-Barron, etc.) clearly shows that this substance is a strong poison of yeast fermentation.

This book, then, is an effective presentation of the facts and procedures of industrial yeast production. Where it fails is in the attempt to place these phases of yeast biology within the framework of fundamental biological principles. Nevertheless, it is an integration of empirical observation and technical experimentation that will reward detailed study by the industrial chemist and by the biologist seeking a reservoir of unexplained observations.

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● GENERAL CHEMISTRY

P. W. Selwood, **Professor of Chemistry, Northwestern University. Revised edition. Henry Holt and Company, New York, 1954. xii + 657 pp. Many figs. Tables. 16 × 24 cm. $6.**

WITH the large number of books currently available for students of general chemistry, choice of a text has almost become a matter of the instructor's attempting to find one which best satisfies his personal preferences regarding the selection and "best" method of presentation of topics. Professor Selwood has developed an interesting book which, subject to the above, certainly contains the necessary features to serve as a satisfactory basic text for the usual first-year college course.

A narrative style is used, with considerable historical background included (perhaps somewhat more than time permits in the rush of the modern course); the subject matter is approached from the atomistic view. The first six chapters deal with Atoms, Atomic Structure, Atomic Combinations (an introduction to valence theory), Chemical Arithmetic, States of Matter, and Molecules (kinetic-molecular theory). These are followed by chapters on Oxygen, Hydrogen, The Chemical Elements, Chemistry and Energy, Solutions, Ionization, Descriptive Chemistry of the various groups of elements, and Electrochemistry. The inorganic section of the book concludes with chapters on Ionic Equilibria, Nuclear Chemistry, and Atomic Power.

The text appears to be free of serious typographical errors. The author has furnished a goodly number of exercises and example problems to assist the student. The "logic" method of solving problems is used with emphasis on the usefulness of the mole concept.

The majority of explanations are quite lucid with only a few exceptions noted, *e. g.*, the discussion of the bond in the hydrogen molecule (fine print on pages 36 and 37). In discussing valence, the author prefers the phrase "highest normal energy level" to the more conventional "valence shell." Electron dot formulas are introduced in the early chapters but are used rather sparingly in sections on descriptive chemistry of inorganic substances. A good introduction to ionization is given. Ionic equations are used very rarely outside the chapters on ionization, ionic equilibria, and electrochemistry. Only a short section, toward the end of the book, is devoted to oxidation-reduction changes as a class of reactions; a very brief discussion of the use of oxidation numbers in balancing oxidation-reduction equations is included in the chapter on sulfur.

A large section (160 pages), approximately the last quarter of the book, is devoted to the chemistry of carbon and organic chemistry. The treatment gives the student a good introduction to organic chemistry and its relation to substances with which he is familiar in everyday living. This seems quite desirable for students in a terminal chemistry course. However, for those planning to take a year of organic later, it provides more material than many teachers may care to use.

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● GMELINS HANDBUCH DER ANORGANISCHEN CHEMIE. SYSTEM 13: BOR. SUPPLEMENT

Edited by *Erich Pietsch* and *Alfons Kotowski.* Eighth edition. Verlag Chemie, GMBH, Weinheim, West Germany, 1954. vii + 253 pp. 28 figs. Tables. 17.5 × 27.5 cm. Paper bound, $33.60. Cloth bound, $34.80.

THIS new version of the Gmelin presentation of boron chemistry is called a supplement, but so much was learned during the period under review (1925–49) that it is nearly twice as long as the 1926 edition and corrects so much of the earlier material as to become virtually a new edition in its own right. Full emphasis is placed upon fields which have sprung into existence, or made relatively great progress, during the past thirty years: the great variety and places of occurrence of boron minerals, the highly developed literature of boron as a trace element necessary to vegetable life, the chemical consequences of boron trifluoride and the BH_2 group (including organic derivatives), incipient knowledge of boron polymers, and the structural principles of the boranes and borides.

The whole presentation is in the well known concise Gmelin style, with the expected highly logical organization and every appearance of thorough understanding of even the most abstract theoretical aspects. The entire attitude is to omit nothing which the literature has to offer, although the writers have maintained their own emphasis upon what they regard as most important and have highlighted the opinions which they consider to be most tenable. For example, the Wiberg analogies of B—N to C—C compounds are employed as a basis of organization, with perhaps too little recognition of the sharp chemical differences between corresponding compounds. At many points one finds accurate presentations of pioneering ideas which were ill-chosen even at the time of origin—immediately followed by newer facts which contradict them; and indeed some especially important corrections have been made by footnote references to work published during the past four years. However, it is unfortunate that the presentation of the chemistry of the boron hydrides and their

derivatives still includes some fantasies, a realistic view of which could have been achieved only through a full study of the literature beyond the year 1949. This situation, taken with the greatly accelerated pace of research in this field, seems to require another edition of boron chemistry in the Gmelin manner within the next ten years. In the meantime, consultation of the present supplement should be the first step taken by any investigator who wishes to make a thorough and critical study of any aspect of the subject.

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• PROGRESS IN BIOPHYSICS AND BIOPHYSICAL CHEMISTRY. VOLUME IV

Edited by *J. A. V. Butler* and *J. T. Randall*. Academic Press, Inc., New York, 1954. viii + 339 pp. Illustrated. 16 × 25.5 cm. $9.50.

In the preface to Volume I of this series the editors state that they"...have had some difficulty in deciding what is the proper field to be covered by reviews of recent progress in biophysics." This volume, like its predecessors, proves that the question was resolved so as to encompass those areas of the literature properly neither biochemistry nor physiology but the "vast and rather amorphous field" where methods of physics are applied to the study of molecules of life or to an elucidation of living structures. Anyone who has attempted to set the limits of biophysics could hardly dispute the decision for its breadth of admission. He might suggest, however, that some investigations concerned with functional aspects of the living organism be included without infringement on other disciplines.

A comprehensive and critical analysis of "Polyelectrolyte gels" by A. Katchalsky gives a good background for better understanding of mechano-chemical engines of the type postulated for muscle by Morales and Botts. Some sophistication in the field is demanded of the reader.

In "The transference of the muscle energy in the contraction cycle," H. H. Weber and Hildegard Portzehl discuss the recent work with muscles, fiber models, and thread models aimed at explaining the role of adenosine triphosphate in contraction. The authors succeed admirably in summarizing and evaluating current developments in this rapidly advancing area of investigation.

H. Fernandez-Moran reviews in "The submicroscopic structure of nerve fibers" the contributions to present knowledge of nerve ultrastructure made possible by examination with the electron microscope. As a necessary background for the newer studies, pertinent results with the light microscope, polarized light, X-ray diffraction and other methods are included.

"The nucleoprotein complex of the cell nucleus, and its reactions," by P. F. Davison, B. E. Conway, and J. A. V. Butler, is concerned with (*a*) methods of isolation, (*b*) physico-chemical properties, (*c*) composition, (*d*) role, and (*e*) action of chemicals and ionizing radiations on this important constituent of living matter. Unfortunately, parts of this paper are not clearly written.

A brief survey of "Chromosome breakage," by P. C. Koller, combines sufficient background material with a clear analysis of recent work with both chemical and physical mutagens to make this one of the most profitable papers of the volume for the non-expert to read.

J. C. Kendrew, in the succeeding chapter, presents a timely discussion of "The crystalline proteins: recent X-ray studies and structural hypotheses" which of necessity assumes knowledge of basic crystallographic theory. Even in the absence of such knowledge, his assessment of results achieved by X-ray analysis of globular proteins represents a significant contribution to the review literature.

The concluding article entitled "Facts and theories about muscle," by D. R. Wilkie, brings up to date many of the aspects of muscle action one usually finds in textbooks of physiology. In addition five recent theories, four of them published since 1950, are critically evaluated. The author makes no attempt to pass judgment on their ultimate value but he suggests a number of ways in which each theory can be experimentally tested.

Each contribution contains excellent illustrative material and few typographical errors remain. This volume should find wide appeal for workers active in the fields represented and for those interested in current developments in these areas.

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• THE ART AND ANTIQUE RESTORERS' HANDBOOK

***George Savage*. Philosophical Library, New York, 1954. vi + 140 pp. 14 × 21 cm. $4.75.**

This alphabetically arranged handbook has more than 250 listings covering such diverse subjects as restoration of paintings, forcing of locks, ultraviolet light, and a test for the presence of sulfate. Naturally, a great deal of interesting material is included both as to materials used in works of art and materials and methods for restoring them, and it is unfortunate that the book cannot be recommended. The author appears to be trained neither in restoration nor in science, and this lack of definite knowledge and experience is too often evident.

On the jacket the publishers speak of the author's "unique knowledge of chemistry." It appears to be "unique" but hardly in the manner that the publishers meant. While the confusion in regard to chemistry might, in many cases, be overlooked, some of the advice in regard to restoration is more serious. His advice in regard to cleaning bronze coins, for example, would or should horrify any antiquarian. Quoted in full it is as follows: "COINS, BRONZE, TO CLEAN. To remove the limestone deposit often to be found covering Greek and Roman coins, coat any visible bronze with paraffin wax and dip the coin into concentrated nitric acid. Note the effect of the acid on the deposit. The time needed to remove it varies somewhat with its nature. When clean, remove wax and wash thoroughly in running water. If the deposit will not yield to nitric acid, other acids may be tried."

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• GENERAL CHEMISTRY

***Edwin C. Markham*, University of North Carolina, and *Sherman E. Smith*, University of New Mexico. Edited by *Herman T. Briscoe*, Indiana University. Houghton Mifflin Company, Boston, 1954. x + 613 pp. Figs. and tables. 17 × 24 cm. $6.**

The writer concurs in the editor's belief that a student may use this text to teach himself. The authors have emphasized principles rather than descriptive details. They hope that this radical departure from the classical method of presentation will hold the interest of the student who has completed a high-school chemistry course. The book is, however, addressed to the student who has had no previous training in chemistry. It is rather optimistic to believe that one lacking in chemical training will find this text "easy going."

Each of the 54 chapters is intended for one lecture assignment. Split assignments of the more difficult chapters, together with the usual reviews and tests, should round out a full year's work in general chemistry. Placing the most important topics first in each chapter is a commendable procedure. The usual number of first edition errata occur, but are easily corrected from the list

accompanying the text. Format is excellent, with double columns and easily read type. Bold-type numbering of subtopics facilitates assignment and cross reference. Judicious use is made of good, modern photographs. The book is profusely illustrated with well-placed, meaningful, and easy to understand charts. Data tables are easily understood and their limited use avoids the appearance of a dictionary-type text.

The authors have drawn extensively from THIS JOURNAL'S valuable store of chemical literature. Fifty per cent of the nearly 200 references are from this one source. Practically all of the references should be found in the average college library. Summaries are sometimes lacking and at times may be mistaken for additional subject content. Each chapter is, however, followed by an excellent set of questions and problems, which tend to summarize the important topics. Placing of organic and colloidal-chemistry chapters at the end of the text may be criticized by those who assign work by successive chapters.

In the first half of the text, theoretical and descriptive contents stand in a five to one ratio, while the reverse is true for the remainder of the book. This conforms to the procedure followed in the usual first-year college course. The unconventional grouping of metallic compounds "according to their non-metallic constituents" may be questioned, although this has always been the basis of the usual qualitative analysis procedure. This classification should be placed earlier in the text in order to be of maximum service to the laboratory work. For the engineering student, this method also lacks information concerning the metals.

The historical aspect has been held to a minimum and is only used to enliven theoretical discussions. The authors' backgrounds in physical chemistry are reflected in their clear and concise treatment of theory.

This is a very teachable text. Its clear and logical presentation of theory, together with the many easily understandable diagrams, and its modern approach to chemical practices should win favor with both instructors and students.

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● EINFACHE VERSUCHE AUF DEM GEBIETE DER ORGANISCHEN CHEMIE

A. F. Holleman. **Revised by *Leonhard Schuler.* Seventh edition. Walter de Gruyter and Co., Berlin. xx + 171 pp. 14 × 22 cm. Pressboard covers. DM 7.20.**

THE death only a few months ago, at advanced age, of the grand old man of chemistry in the Netherlands, is recalled by the appearance of this latest edition of one of Holleman's famous educational works, in a sequence long since entrusted to younger hands. The "Versuche" is a laboratory manual for beginners. Apparently three editions have now been handled by the junior author.

Despite the general availability of elegant new types of apparatus, the author makes a special point of retaining simplicity of equipment. He is evidently trying to cater to minor institutions of higher education, and also to individuals engaging in self-instruction. Chromatography, standard-taper ground-glass devices, and fancy new reagents are out. Although economic restrictions in convalescent Germany may be significant, conservatism in avoiding modern luxuries seems to have been overdone. Almost the entire list of materials (pages xv to xix) could have been found in a pre-World-War-I storeroom. For example, higher homologues such as inexpensive propyl and butyl alcohols, long used to advantage in America, are bypassed. One must concede, however, that this is a scholarly work and that a lot of organic chemistry has been packed into the tersely written 171 pages.

The many synthetic experiments might be described as semi-preparative, on a scale varying from semimicro to values approaching macro size. No great attention is paid to completeness of reaction, serious purification, or calculation of yield. A large number of the experiments are qualitative tests. In America such a manual would most likely employ the blank-form pattern, but the present volume has no such suggestion. Equations are generally presented. Description of general technique is brief, with no attempt made at systematic qualitative organic analysis. To be sure, an abundance of raw material for such analysis is presented. In general, this manual would probably not be adopted for the main doctoral-training course characteristic of a European university, but rather in institutes of applied science and perhaps by the German equivalent of the junior college.

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● GMELINS HANDBUCH DER ANORGANISCHEN CHEMIE. SYSTEM 10: SELEN. PART A3

Edited by *Erich Pietsch.* Eighth edition. Verlag Chemie, GMBH, Weinheim, West Germany, 1953. xvii + 184 pp. 17.5 × 25.5 cm. 158 figs. $26.64. (Available through Walter J. Johnson, Inc., 125 E. 23rd St., New York 10, N. Y.)

WITH the appearance of this section, dealing with the selenium rectifier and photocell, Part A of System No. 10 has been completed. The previous sections covered the historical aspects, the occurrence, formation, and preparation of the element in its several modifications, including colloidal selenium; the physical, chemical, and electrochemical properties, as well as the detection and determination of the element. The electrical properties, and especially the photoelectric characteristics of selenium, were discussed in part, and the present volume completes this discussion.

In recent years the rapidly increasing application of the selenium rectifier in various industries has been an outgrowth of extensive research which has been devoted to the study of the semiconductor rectifiers. In the present work, about 60 per cent of the book is devoted to the rectifier; the remainder is concerned with the photocell. Chapters on general electrical properties, technology, manufacture, and technical application of the rectifier are followed by 40 pages dealing with the theory underlying its operation.

In the remaining chapter on the selenium photocell, the electrical and optical properties are discussed in detail, followed similarly by accounts of the technology, applications, and theory of the cell. The literature coverage for Section 3 of Part A is stated to be through 1952, whereas in Sections 1 and 2 the coverage was through 1939 and the middle of 1949, respectively.

WALTER C. SCHUMB

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● THE PSYCHOLOGY OF INVENTION IN THE MATHEMATICAL FIELD

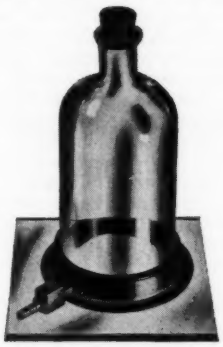
Jacques Hadamard. **Reprint. Dover Publications, Inc., New York, 1954. xiii + 145 pp. 14 × 20.5 cm. Paper bound, $1.25. Cloth bound, $2.50.**

THIS is a reprint of the first edition, which appeared in 1945. In the introduction the author says he really means "discovery" rather than invention. Thereafter the discourse is on various aspects of the "scientific method," some of which will be apparent from a few of the chapter headings: Discussions on Unconsciousness; The Unconscious and Discovery; The Later Conscious Work; Discovery as a Synthesis; Paradoxical Cases of Intuition. The scientific method is not always the simple, straightforward process that some people suppose.

Out of the Editor's Basket

Filter Bell and Slide Valve

Among recent developments at the New York Laboratory Supply Co., Inc., is an improved accessory for laboratory filtration work. Their "Filter Bell" is now equipped with a completely redesigned Slide Valve in which flat ground surfaces make a vacuum-tight closure, permitting application or release of vacuum in the bell jar while retaining vacuum in other interconnected parts of a filtration system. The Filter Bell has been further improved to provide a better closure all around. It is now being supplied with a glass plate to provide its bottom rubber gasket with a good surface against which to make a tight seal; the top also has been redesigned so that a rubber stopper may be used, giving firmer support to a funnel.



The Slide Valve also has general utility alone and may be utilized in conjunction with ordinary filter flasks in the same manner as with the Filter Bell.

Details may be had by writing New York Laboratory Supply Company, Inc., 76 Varick Street, New York 13, N. Y.

New Versatile Laboratory Stirrer

Eberbach's new 3-Speed Stirrer offers laboratories the "Hollow Spindle" and continuous, light duty operation at 500, 750, or 1000 r.p.m. The 1/50 h.p. split-phase, induction motor by Bodine develops 4 inch-pounds of torque. Stirrer is driven by V-belt on 3-step pulleys.

Motor and stirrer are mounted on a 2-piece frame adjustable to maintain V-belt tension. The Hollow Spindle firmly grips stirring rods from $^{7}/_{32}$ to $^{5}/_{16}$ in. by an adjustable chuck and spring clip. These center the agitator and allow rapid change of its working length. Complete information in Bulletin No. 490 Eberbach Corporation, Ann Arbor, Michigan.

Amperometric Titrimeter

Fisher Scientific Company, 717 Forbes Street, Pittsburgh 19, Pennsylvania, has announced the availability of a new amperometric accessory to its Electropode, a low-priced manual polarograph.

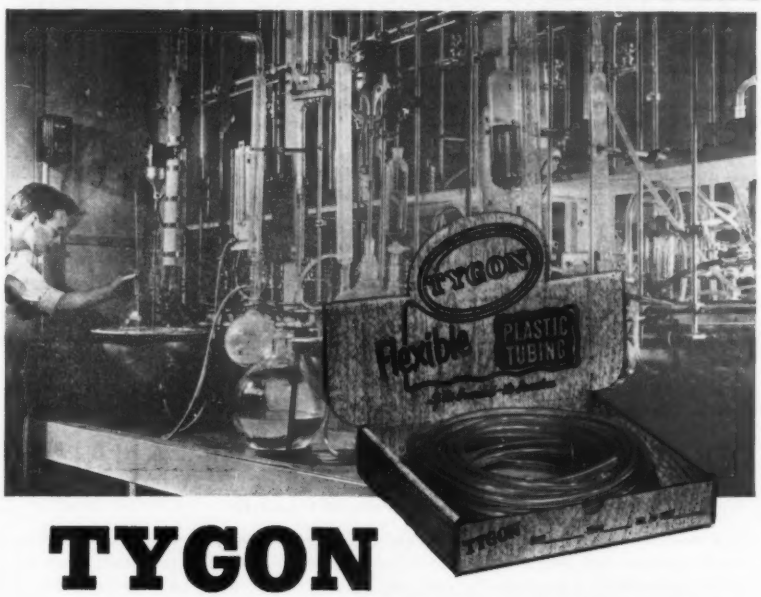
With the Amperometric Titrimeter, traces of such impurities as cadmium, copper, zinc, lead, antimony, or arsenic can be "picked out" in complex alloys, and essential components such as chromium, cobalt, nickel, manganese, vanadium, or titanium assayed with precision—often, it is said, in solutions as dilute as 0.000001 *N*.

Chloride and bromide can be isolated from other halides, and cyanide, phosphate, chromate, sulfate, and many other ions found by titration where other methods fail. Numerous organic compounds can be determined directly.

Vacuum Gauge

The Model 515 "Alphatron" Vacuum Gauge indicates pressures from 1 micron (0.001 millimeter) to 10 millimeters of mercury. The pressure is read from a single four decade logarithmic scale; no switching from one range to another is necessary. The gage is small, rugged, and portable, requiring only a source of 110 volt 60-cycle alternating current. It is manufactured by The Equipment Division of National Research Corporation.

Like other NRC "Alphatron" vacuum gages, the Model 515 gage utilizes a sealed radium source; this emits alpha particles



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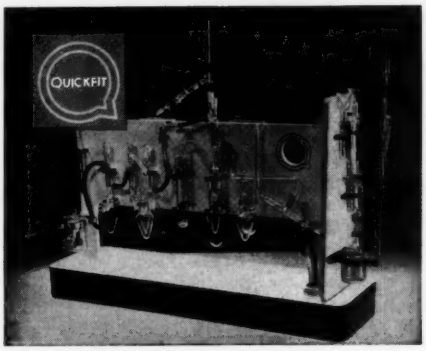

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Various types of current observed in polarography (residual, absorption, migration, diffusion, kinetic and catalytic) are treated extensively and each is illustrated by simple experiments which can be carried out in any student laboratory. Dr. Müller shows how to distinguish between these types of currents and how to recognize diffusion, kinetic and catalytic currents by varying the drop-time or -size of the mercury electrode.

The author has presented a new approach to the problem of polarization of an electrode which may have some value for student instruction. Detailed discussion of this problem includes directions for testing the non-polarizability of an electrode.

Rather than enumerate a number of detailed analytical procedures, Dr. Müller has given the principles on which these are based, with sufficient instruction to enable anyone to develop his own, or carry out a published analytical procedure. Following the given directions, no one should find it difficult to test the polarographic reversibility of a reaction or to determine the coordination number of a complex metallic ion.

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and produces ionized gas molecules which are collected on a plate to produce a current indicating directly the measured pressure. The gage cannot be damaged by exposure to atmospheric pressure because the ion source operates at room temperature and at zero potential. "Alphatron" Vacuum Gauges are also less susceptible to contamination than are hot element vacuum gages. Additional information is available from Naresco Equipment Corporation, Dept. JCE, 160 Charlemont Street, Newton Highlands 61, Massachusetts.

Isotope Analyzer

The Model ISA Isotope Analyzer, recently announced by the Forro Scientific Company, 833 Lincoln Street, Evanston, Illinois, is designed to perform rapid and accurate qualitative and quantitative analysis of isotope mixtures containing beta emitting components. The technique is based on the absorption and scattering of beta rays in materials of high atomic numbers as described in *Zeitschrift für Physik* **138,** 441 (1954).

The instrument is said to be several times as sensitive as beta spectroscopes. Three different models of the unit are available, with the minimum activity of an isotope necessary for its detection being 4×10^{-9}, 1.2×10^{-9} curies, and 0.2×10^{-9} curies. The Isotope Analyzer may be operated with any commercial scaling unit having a 0.25 volt input sensitivity and a high voltage supply.

Distilled Water Heater

Barnstead engineers announce a new aid for laboratories that require hot distilled water. This new product from the Barnstead Still & Sterilizer Company keeps hot distilled water on tap for instant use. The water is maintained automatically at any predetermined temperature by means of an adjustable thermostat. This heater not only saves time and bother of heating in beakers but also maintains the desired temperature level. Tank is constructed of tinned copper and has removable cover.

Exterior finish is satin nickel plate. The Barnstead Heater has a $1^1/_2$ gallon capacity. A pilot light shows when current is on. Dial type thermometer 30° to 240°F. Heating unit 650 watts. Further information may be had by writing Barnstead Still & Sterilizer Co., 108 Lanesville Terrace, Forest Hills, Boston 31, Massachusetts.

Test Tube Caps

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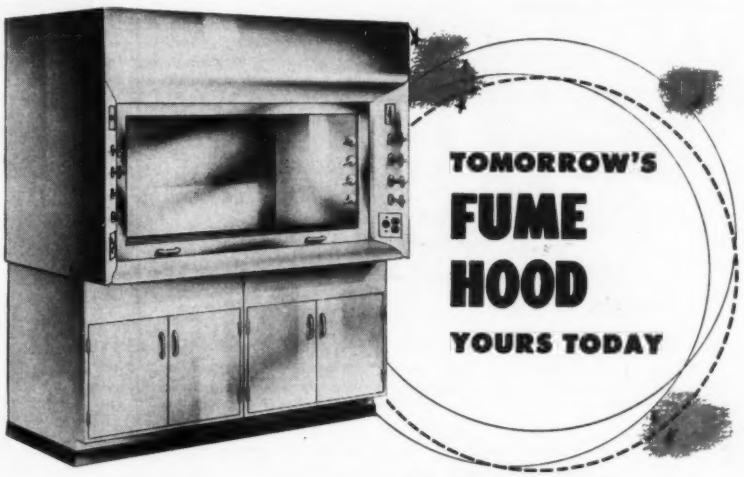
Brochure containing detailed information available from the Lowell S. Fisher Company, Box JCE, 31 East 45th Street, Indianapolis 5, Indiana.

X-ray Spectrograph

A new Norelco Autrometer, an automatic multi-element indexing X-ray spectrograph that gives percentages of as many as twelve elements in a specimen in a range of over 71 elements in the periodic table, has been announced by the Research and Control Instruments Division, North American Philips Company, Inc., 750 South Fulton Avenue, Mount Vernon, N.Y.

Permanent Cartridge Type Demineralizer

The Perma-Demon is a new inexpensive demineralizer just developed by Enley Products, Inc., 1236 Broadway, Brooklyn 21, New York. The unit consists of a cartridge of clear unbreakable tubular plastic with removable top; built-in carborundum porous stone filter and fiber glass screen; rubber hose for both inlet and outlet connectors; and aluminum bracket



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- Entire hood is stainless steel, ground and polished to satin finish for easy cleaning and decontamination. Hood exterior and cabinet work of cold rolled, Bonderized steel with baked enamel finish.
- Working surface of 14 ga. stainless steel, supported by structural steel grating, allows use of lead bricks for shielding. Entire surface forms watertight, ⅜" pan to retain spillage. 5" diameter cupsink integrally welded to worktop.
- Service controls for blower, air, gas, water, vacuum and electric current (110v and 220v) located on exterior for remote control.
- ¼" thick safety glass sash is completely framed to protect against breakage—counter-balanced for smooth, easy raising and lowering.
- 84¼" overall height, with base units, accommodates low ceilings. Other dimensions: length 6 ft.; width 38 in. (excluding valve handles).

Write for descriptive literature and drawings on the new Kewaunee 3604 Fume Hood

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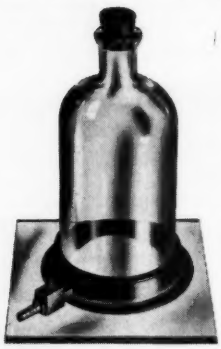

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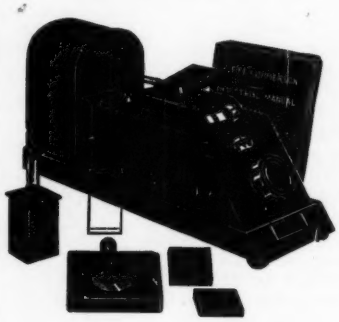

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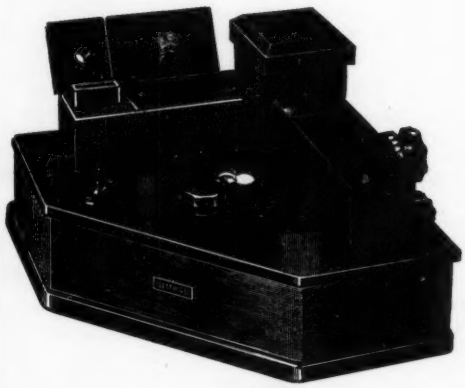

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for attachment to wall. As water flows from the tap into the Perma-Demon, it is claimed that all ionizable impurities are removed resulting in water of a high purity. The ion exchange material is easily removed and replaced.

Laboratory Heat Transfer Unit

For quite some time there has been a demand for a heat transfer system of small size for laboratory and pilot plant use. Recently introduced is the "Beth-Tec" EH series heat transfer unit using duPont "Hi-Tec" eutectic salt as the circulating medium. Temperatures ranging from 650°–1000°F. may be easily reached without pressure with this heat transfer unit which was developed to approximate plant conditions in a laboratory size unit.

The Beth-Tec is an integrated process unit, complete with salt tank, electrical salt heaters, circulating pump, and instrumentation for safety and control. Several standard sizes are available ranging from a heating output of 10,000 B.t.u./hr. to 250,000 B.t.u./hr.

Complete details are available from Bethlehem Foundry and Machine Company of Bethlehem, Pennsylvania.

Oscilloscope Camera

A new High Speed 0.35 mm. camera for continuous recording of oscilloscope traces, the Model OC-1 is announced by Brea Instruments. Weighing only 6 pounds, with a film capacity of 100 feet, the camera may be mounted directly on the bezel of any 5 inch oscilloscope. The illustrated installation features simultaneous binocular viewing and recording, illuminated identification card, and flashing lamp time reference.

The film transport rate may be set between 1 and 300 inches per second by means of a continuously variable remote motor control. Lower speeds can be achieved by gear substitution and higher speeds up to 400 inches per second can be reached with special starting acceleration control. Less than 15 seconds are required for removing exposed film and reloading with daylight loading spools. The film consumed in starting or stopping at maximum speed is less than two feet.

A choice of f/1.5 or f/2.8, 50 mm. coated lens with iris diaphragm is offered, giving an image reduction ratio of 4.5 in the usual 5 inch oscilloscope installation. Available as an accessory is a variable delay timer which permits an event to be initiated from 0.5 to 5 seconds after the camera has started. Address inquiries to Mr. L. J. Cannon, Brea Instruments, P.O. Box 248, Brea, California.

New Literature

● The United Carbon Products Company, has just announced the publication of a modern catalogue of graphite electrodes for the Spectroscopic profession. Now coming off the press, this new catalogue contains a wealth of information and specifications on Spectroscopic Preformed Custom Electrodes, the new Platrode Series, Ultra Pure Graphite Rods and Powders.

It is believed that this new UCP catalogue represents the largest selection of Spectroscopic Electrodes ever compiled in one volume. Reference is made, in each case, to the particular merit of each design

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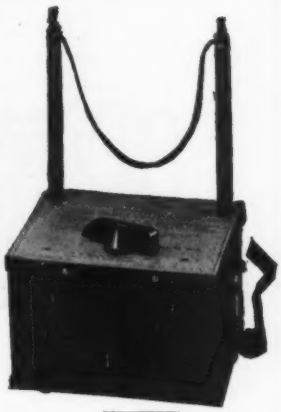

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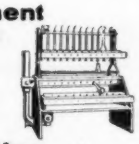

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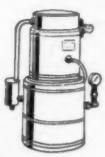

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and its most acceptable usage. Specification information is complete in all cases and provision is made to submit designs for custom made electrodes. Valuable information on graphite machining, purification, and protection appears throughout the catalogue. A comprehensive Reference List is included as valuable source material. United Carbon Products Company, Bay City, Michigan, will send this new catalogue without obligation.

● Higher living standards and the increased competition for the consumer's dollar is making it practically a must for even the *smallest processor or manufacturer* to take a look at the growing technology around him according to a how-to-do-it booklet, "Quality Control and Research—insure your product in tomorrow's market" published today.

The booklet, a project by the Scientific Apparatus Makers Association's laboratory apparatus and optical sections' public information committee, points out further that, "volume buyers on the American scene are constantly increasing their demands upon the manufacturer for goods that are produced according to the specification."

"Recent revision of the federal tax law also favors initiation of more quality control and research. Smaller firms, especially, will be helped by Section 174 of the new Internal Revenue Code permitting investments in research and experimentation to be deducted currently," the booklet points out.

To partially cover the cost of printing and mailing, copies of the SAMA booklet are available at twenty-five cents each when requested on a business letterhead from the Scientific Apparatus Makers Association, 20 North Wacker Drive, Chicago 5, Illinois.

● Chromatographic Experiments with Aluminum Oxides—Woelm is available from Alupharm Chemicals, 54 C Street, Elmont, L. I., New York. This booklet gives some specific examples of the use of this technique which whould show the beginner the ease, as well as let him see the vast potential of chromatography.

● A new and accurate method of cutting the electrode standing time in multiple soil pH determinations has been developed by the Department of Soils, Ontario Agricultural College, Guelph, Ontario. Annually the department makes some 25,000 soil pH measurements, thus creating a need for shortening these determinations to the utmost.

Ordinarily from 5 to 15 minutes are required for the pH meter electrodes to stand in the soil solution. The new method, involving the use of a Beckman Model H-2 pH meter, cuts this time down to 20 seconds or less, and eliminates the need for a fixed soil-water ratio.

A complete description of the method employed by the Ontario Agricultural College may be obtained by writing for Data Sheet 25-36, Beckman Instruments, Inc., Fullerton 1, California.

● In a new four-page list of compounds available, Bio-Rad Laboratories, 800 Delaware Street, Berkeley, California, includes a helpful alphabetical index of compounds, including alternate nomenclature, and providing index numbers to loca-

NEWS from FILTERTOWN

The use of E&D filter papers is intriguing. One project that we recently learned about was concerned with the filtration and reduction of dirt for the purpose of reconstructing climatological data. . . . E&D grade 301 is extensively used in research dealing with electrochematographic sequences. It is available in two thicknesses. One, is .030 inches. The other, is .052 inches. And like all E&D papers it is also available in many sizes and shapes. . . . Folded circles were originated in the E&D laboratories many years ago. A special method of folding enhances rapidity and prevents tearing at the point. You can get E&D folded circles up to 24 inches in diameter. Our authorized distributors carry them in stock for prompt delivery. . . . E&D is the only company in America exclusively engaged in the manufacture of filter paper for science and industry. Your questions, comments and suggestions are extremely welcome. Our backlog of "know how" can be of help to you, and we will gladly try to cooperate in finding the right filter paper for you. . . . For free samples of E&D filter papers, write to T. J. Druding. . . . And for determining the right grade for use in industrial filtration problems write for Filtration Analysis Report.

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tion in the chemical classification list. The compounds listed include simple carbon compounds, alcohols and derivatives, acids and derivatives, amino acids, purines and pyrimidines, miscellaneous compounds, and nitrogen-15 labeled compounds.

● The latest developments in high-pressure equipment for pressures to 100,000 p. s. i. and temperatures to 1000°F. are presented in the 1955 Edition of Catalog 406, published by the American Instrument Co., Silver Spring, Maryland. The high-pressure equipment described in the new catalog embraces pilot plants, reaction vessels, valves, fittings, tubing, pumps, compressors, pressure balances, instruments, and accessories. Catalog 406 is available, upon request, without charge.

● "The JAco Ebert Plane Grating Spectrograph with Order Sorter" has just been published by Jarrell-Ash Company. The catalog illustrates and describes in detail this truly new instrument—the first spectrograph that is adapted to all spectra, from the simplest to the most complex. Of special interest is the section devoted to the description of the Order Sorter—a unique JAco-developed tool that provides wide wave-length coverage and good speed at high dispersion and resolution.

Readers who desire a copy of this new literature which is identified as Catalog EB-10-54, may secure a copy by writing Mr. Richard Ashley, Jarrell-Ash Company, 26 Farwell Street, Newtonville, Massachusetts.

● Scientific Apparatus and Methods, Volume Six, No. 3, is now available from E. H. Sargent and Co., Dept. JCE, 4647 West Foster Avenue, Chicago 30, Illinois. Featuring "Thermistors as Better Thermometers" and "Precise Oscillometric Analysis of Two-component Single Phase Liquids" as well as some catalog revisions.

● "The Story of Employment Opportunities" is the title of a new, interesting illustrated booklet on the nature of the chemical industry and its contributions to the welfare of our nation. Some consideration of research and the role it plays in developing new jobs. Also an excellent discussion of the time motion studies made by employers today in order to increase output. The Public Relations Department of E. I. Du Pont de Nemours & Co., Wilmington, Delaware, will furnish this booklet on request.

● Two booklets have come to our attention, "Experiments with Gas" and "Advanced Experiments with Gas." They contain an excellent array of experiments, for students at the junior and senior high-school levels, respectively. They were prepared under the direction of one of our editorial group, Elbert C. Weaver, and teachers should find them very useful. They are described as "classroom experiments using gas," and the booklets may be obtained free from the Educational Service Bureau, American Gas Association, 420 Lexington Avenue, New York 17, New York.

● Practical Refractometry by Means of the Microscope, by Roy M. Allen; 76 pages, 15 figures, published by R. P. Cargille Laboratories, Inc., New York 6, New York, $1.00. A text on the determination of indices of refraction of solids by microscopical methods. Elementary

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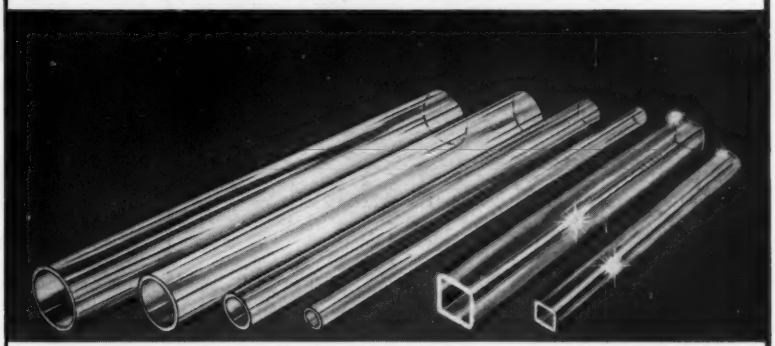

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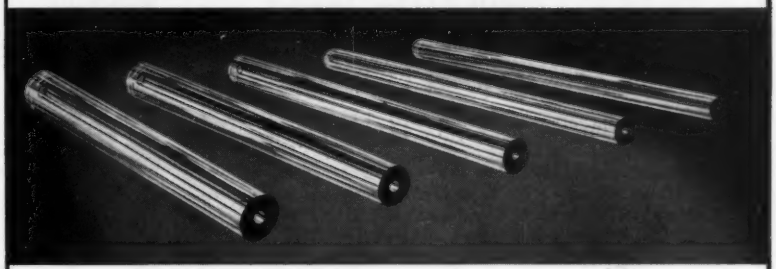

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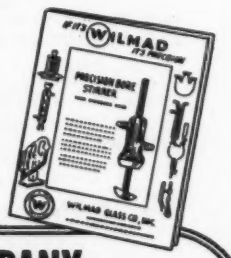

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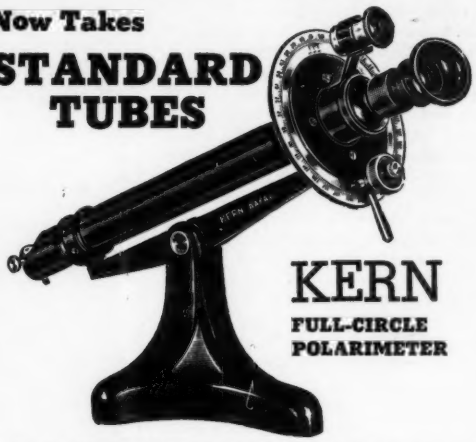

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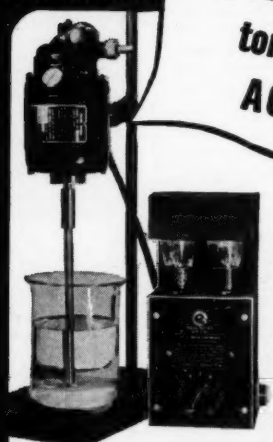

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● "Chemistry of Steel," a well illustrated booklet and a new color filmstrip on this topic, has been especially prepared for high-school chemistry classes by a group of Cleveland teachers and the American Iron and Steel Institute, 350 5th Avenue, New York 1, New York.

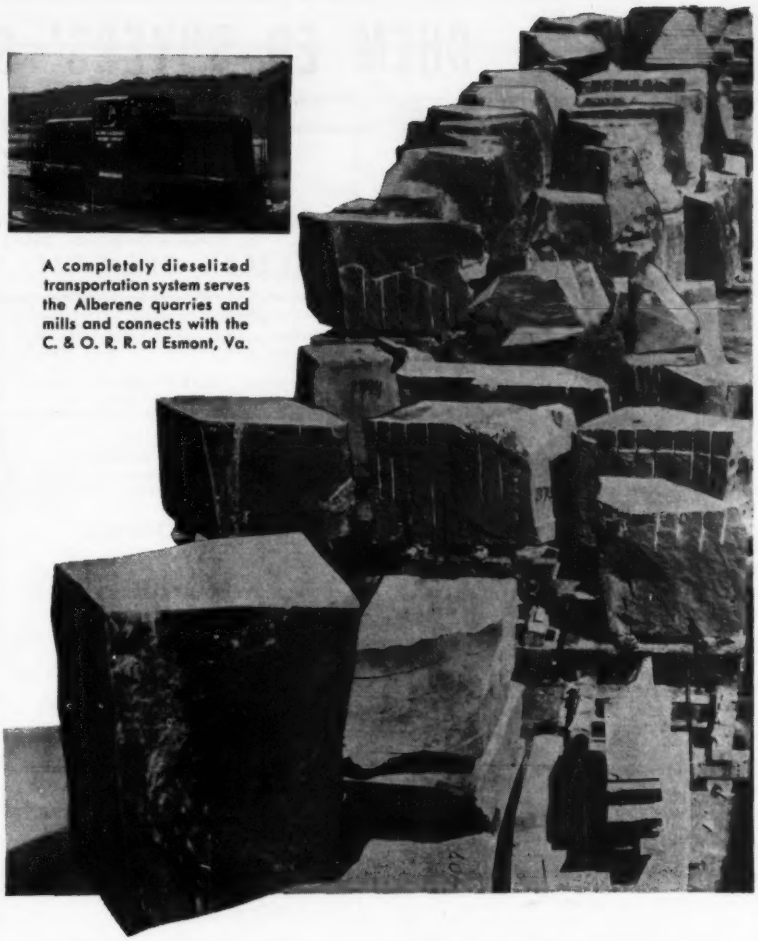
● The 1955 edition of the booklet, "Physical Properties of Synthetic Organic Chemicals," has just been issued by Carbide and Carbon Chemicals Company, a Division of Union Carbide and Carbon Corporation. In 24 pages, this edition presents the latest data on more than 350 organic chemicals. Copies of this booklet (F-6136) are available without charge from Carbide and Carbon Chemicals Company, 30 East 42nd Street, New York 17, New York.

● 'How Temperatures Are Measured," by G. M. Wolten is an interesting informative discussion about a topic about which there is a great deal of misunderstanding and confusion. Available from Tempil Corporation, 132 West 22nd Street, New York 11, New York.

● Details of a new research camera system using synchronized-streak techniques to produce a writing speed of 5.46 millimeters per microsecond and a sweep duration of 44 microseconds, are given in a new folder, Form 168-754. Beckman & Whitley, Inc., 838 E. San Carlos Avenue, San Carlos, California.

● The Electric Hotpack Company, Dept. JCE, 5097 Cottman Avenue, Philadelphia 35, Pennsylvania, has a new four-page bulletin "Prescription For Your Constant Temperature Problems" illustrating 11 typical histories and their solutions.

● A 24-page booklet which summarizes information on the major established uses of phthalic anhydride has been prepared by Monsanto Chemical Company's Organic Chemicals Division. Also they have added four new acrylonitrile derivatives to their group of nitrogen petrochemicals. The new compounds are β,β'-thiodipropionitrile, β,β'-oxydipropionitrile, β-chloropropionitrile, and β-chloropropionic acid. All are available in experimental quantities. Monsanto Chemical Co., St. Louis 4, Missouri.



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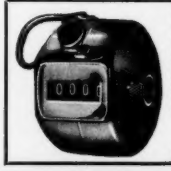

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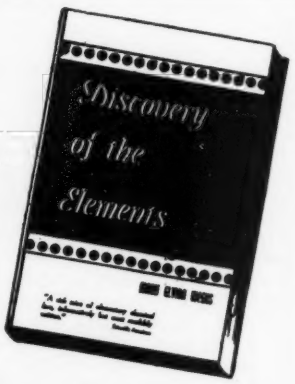

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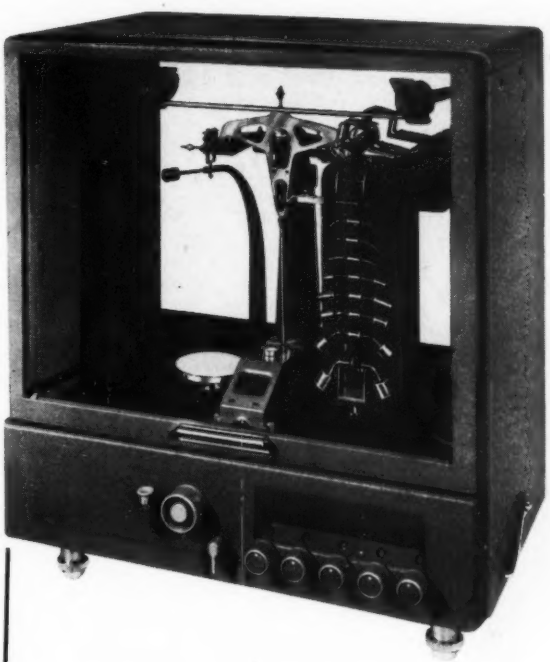

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